TRANSACTIONS OF THE AMERICAN SOCIETY FOR METALS

DECEMBER, 1935

Volume XXIII Number 4

The TRANSACTIONS *of the*
AMERICAN SOCIETY FOR METALS

Published quarterly and Copyrighted, 1935, by the AMERICAN SOCIETY FOR METALS
7016 Euclid Avenue, Cleveland, Ohio

SUBSCRIPTIONS: (members) $2.50 per year
(non-members) $5.00 per year, $2.00 per copy
Foreign (non-members) $6.50 per year, $2.50 per copy

Entered as second class matter, November 9, 1931, at the Post Office at Cleveland, Ohio, under the Act of March 3, 1879

RAY T. BAYLESS, *Editor*

Vol. XXIII | December, 1935 | No. 4

The object of the Society shall be to promote the arts and sciences connected with either the manufacture or treatment of metals, or both.

Officers and Board of Trustees

R. S. ARCHER, President
Republic Steel Corp., Chicago

E. C. BAIN, Vice-President
U. S. Steel Corp., N. Y. City

W. P. WOODSIDE, Treasurer
Climax Molybdenum Co., Detroit

W. H. EISENMAN, Secretary
7016 Euclid Ave., Cleveland

TRUSTEES

B. F. SHEPHERD, Past President
Ingersoll-Rand Co., Phillipsburg, N. J.

WALTER MATHESIUS
Carnegie-Illinois Steel Corp.
Chicago

R. L. KENYON
American Rolling Mill Co.
Middletown, Ohio

GEORGE B. WATERHOUSE
Massachusetts Institute of Technology
Boston

S. C. SPALDING
American Brass Co.
Waterbury, Conn.

Publication Committee

W. P. SYKES, Chairman — Cleveland
RAY T. BAYLESS, Secretary — 7016 Euclid Ave., Cleveland

Members:

H. E. Ardahl, Tri-City '37
C. L. Clark, Detroit '36
C. N. Dawe, Detroit '38
W. E. Harvey, Philadelphia '37
G. V. Luerssen, Lehigh Valley '36
O. W. McMullan, New York '38
N. I. Stotz, Pittsburgh '38
A. A. Bates, Cleveland '38
E. S. Davenport, New Jersey '37
M. A. Grossmann, Chicago '37
Louis Jordan, Washington '36
D. F. McFarland, Penn State '37
R. F. Mehl, Pittsburgh '36
Joseph Winlock, Philadelphia '37

THE IMPORTANCE OF ALUMINUM ADDITIONS IN MODERN COMMERCIAL STEELS

By Harry W. McQuaid

Abstract

From an addition, primarily made to quiet "wild" heats and supposedly harmful in its final effect, aluminum has become the most important factor in the production of heats of steel having uniform characteristics of hardenability, grain-size, etc.

The development of the carburizing test for grain-size and normality gave a means for relating variation in hardening characteristics to steel-making practice with the result that the steel user could place on the steel maker the responsibility for much of the variation in his processing. This variation became of great importance with the development of mass production and continuous heat treating equipment, resulting in an insistence on steel having uniformly the inherent characteristics best suited to the production of a given part.

The resulting developments in steel-making practice and the part played by aluminum are discussed.

The effect of the aluminum addition on the properties of plain carbon steel is shown, indicating a relation between such properties as grain-size, hardenability and pearlite divorce on the aluminum addition.

Whether the aluminum acts directly or indirectly to cause the variation in characteristics is discussed and an hypothesis is offered suggesting metallic aluminum in solution and its effect on carbide coalescense as a cause of grain growth inhibition and pearlite divorce.

Introduction

THE Campbell Memorial Lecture, which this Society has so fittingly established in honor of Professor Edward De Mille Campbell, has attained a standard of excellence befitting his position as an educator and a scientist, and these lectures have been masterpieces in the field of true instructive discourse. While your speaker is deeply appreciative of the great honor bestowed on him as your selection for the Tenth Annual Campbell Memorial Lecturer, he is

This is the Tenth Edward De Mille Campbell Memorial Lecture, presented by Harry W. McQuaid, metallurgist, Republic Steel Corporation, Massillon, Ohio. The lecture was presented at the Seventeenth Annual Convention of the Society, held in Chicago, September 30 to October 4, 1935.

however cognizant of his own limited ability as a scientist and particularly as a scientific lecturer. In fact, while due to a happy combination of circumstances he has been almost continuously involved for years in research and development work in almost every phase of the making and using of steel, this work has always been done with an eye directly on the commercial possibilities.

With a background of mill and shop practice rather than laboratory experience, this lecture will differ from those which have preceded it in that more field experiences will be given, more results from commercial practice and probably less of the highly scientific will be presented than perhaps some of you would like to hear in a lecture of the high standard expected of Campbell Memorial Lecturers.

It is also freely admitted here that this lecture is only a brief and in many ways inadequate report covering the work done by many men. In short your lecturer is more of a reporter than anything else and only the wholehearted co-operation of many self-sacrificing men has made this report possible. It will be difficult to give proper and due credit to all who have helped, not only in obtaining the present data but in much of the preliminary work of the past years. It would be difficult to name all who have helped, but among others the names of Yoerns, Motok, Morris, Sergeson, Johnson, Archer and Smith of our company, stand out. To all those who contributed so unselfishly, your lecturer is deeply grateful. Certainly due credit must be given to Ehn, who worked with your lecturer so earnestly and helpfully for two years to determine the reason for the variation in the hardening quality of different heats of steel.

In selecting the subject for this lecture, it was decided to choose a subject of general active practical interest to the steel user and one which was particularly timely. To satisfy these requirements, it was only necessary to select the one of our research and development projects which was most interesting to your speaker and which involved the general study of the effect of variation in steel-making practice on the properties of the finished part; and specifically for the lecture, the effect of small aluminum additions on these properties with which we are primarily interested in the finished part.

It is not expected that this lecture will contain any information which is entirely new to all of you—in fact the original intention was to gather together the known data from the literature and from practice, on the role of aluminum in steel-making. It was believed that a carefully arranged and properly presented discussion of the im-

portance of the aluminum addition to the steel user would be of enough interest to make such a presentation worth while.

In view of the derogative opinion once held by steel makers and users alike of the use of aluminum in the making of steel, it was felt that the time was ripe for a presentation of the true status of this important element in steel-making. It would be closer to the truth, probably, in discussing the former status of aluminum to restrict these derogative opinions to the steel user and exclude in most cases the steel maker.

It was originally believed (and probably true) that aluminum was first used as a corrective for over oxidized heats, and was frowned upon, as being a means for getting by with poor furnace practice. In view of the present widely used, although rather carefully concealed practice of adding aluminum to control hardenability, grain-size, etc., and particularly the combination of aluminum addition with greatly improved knowledge and control of the basic open-hearth furnace itself, it was felt that the status of this element had completely changed in recent years. This change in status is of course important to user and maker of steel alike, and it is hoped the discussion of this new status of aluminum to which this lecture is devoted, will be of general interest.

Much has been written on the subject of variation in the properties of various heats of steel of approximately the same composition as generally analyzed. Much has been written on the effect of grain-size; "normality," etc., on the characteristics of the finished part. Grain-size specification or understandings have become almost universal, especially in the automotive steels but not always with the best of judgment. Some of our most prominent metallurgists have changed from open scorners of grain-size specifications to become the most ardent advocates. Normalizing and annealing cycles are predicated on grain-size specifications. Machining results have governed in many cases the grain-size specifications—and so has distortion in quenching—impact requirements—fracture requirements, etc.

In most cases it has been found that the extremely fine grain very abnormal types have definite advantages when combined with sufficiently high carbon, manganese and other alloys to insure satisfactory quenching. While this is being given considerable publicity at the present time, the advantages of the extremely fine-grained type was early recognized by those closely connected with the application of heat treated alloy steel and the carbon-manganese types.

Grain-size specifications have become so common as to be considered (in this country) a natural requirement where steel-making practice is to a large extent governed by the customer's requirements for a given part, rather than by chemical analysis and soundness tests.

Visitors from abroad who are interested in purchasing steel, and particularly special purpose steel, are amazed at the importance centered in this country on grain-size requirements. They express concern over the fact that European steel producers have not yet reached the rather unenviable position of the American steel producer of trying to guarantee that the steel as shipped will make a given part regardless of design or specified analysis. They do not realize the revolution which has taken place behind the scenes in American open-hearth steel practice to permit the steel maker to take the position noted above. And this revolution has been one not only of open-hearth operation, but also in the viewpoint and policy of the management and sales department as regards obligation to the customer. Few realize the part played by aluminum in this revolution and particularly in its relation to general open-hearth practice and metallurgical control, for aluminum is one of the most difficult of metals to control at steel melting temperature and especially in the presence at these temperatures of the easily reducible metallic oxides.

The development in the control of open-hearth operations required to achieve results with aluminum in order to produce steels of definite heat treating characteristics, has been an achievement of no small moment by the steel mill metallurgists. It is sufficient to say at this point, that this urgent need of improving open-hearth operations to meet the steel user's insistence on a product of uniform characteristics has resulted in improving the basic open-hearth product to the point that it can be made to a quality equal to any other method of producing commercial tonnage steels.

The effect of grain-size variation on the characteristics of the finished steel has been well covered in the past few years. Epstein and Rawdon,[1] Hardy,[2] Bain,[3] Grossmann,[4] Schane,[5] and others have

[1]S. Epstein, H. S. Rawdon, "Steel for Case Hardening—Normal and Abnormal Steel," Bureau of Standards Journal of Research, September, 1928.

[2]T. W. Hardy, "Grain-Size Controls Toughness," *Iron Age*, December 20, 1928.

[3]E. C. Bain, "Factors Affecting the Inherent Hardenability of Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 20, November, 1932, p. 385.

[4]M. A. Grossmann, "Grain-Size in Metals, with Special Reference to Grain Growth in Austenite," TRANSACTIONS, American Society for Metals, Vol. 22, December, 1934, p. 861.

[5]Philip Schane, Jr., "Effects of the McQuaid-Ehn Grain-Size on the Structure and Properties of Steel," TRANSACTIONS, American Society for Metals, Vol. 22, December, 1934, p. 1038.

discussed the importance of grain-size control, but there has been little published data as to the part played by aluminum in this work.

Epstein and Rawdon[1] in their classic studies of normal and abnormal steels were the first to indicate the importance of aluminum in controlling grain-size and normality, and Epstein, Nead and Washburn[6] again at the Grain-Size Symposium of this Society in New York last year pointed out the value of aluminum in this regard.

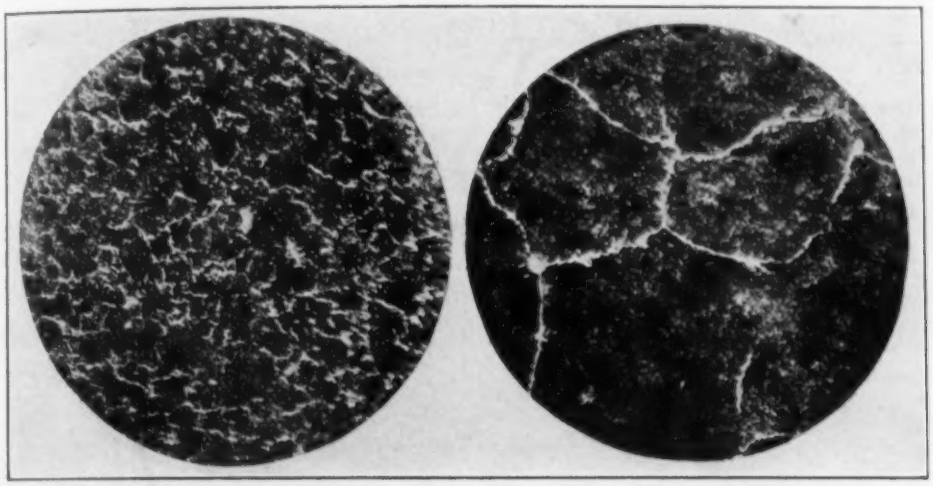


Fig. 1—Fine Grain Obtained by Aluminum Deoxidation as Contrasted with the Coarse Grain of Manganese Deoxidation. Fig. 1 (Left) Hypereutectoid Zone of Specimen from Ingot Deoxidized with Aluminum. Fig. 1 (Right) Hypereutectoid Zone of Specimen Deoxidized with Ferromanganese. × 200.

Both papers were important contributions to the subject of aluminum in steel. Herty and his associates have pointed out several times the difference in characteristics of aluminum and silicon-killed steels. One of the first references to the effect of aluminum deoxidation is found in the paper by Mr. Ehn and your lecturer in 1922[7] in which the fine grain obtained by the aluminum deoxidation is contrasted with the coarse grain of the manganese deoxidation. (Fig. 1)

Most of the investigators, to date, have been concerned with the general effect of aluminum on grain-size and deoxidation results in a general way, and have accepted without much question that oxide dispersion is the reason for the aluminum addition other than for straight deoxidation.

---

[6]S. Epstein, J. H. Nead and T. S. Washburn, "Grain-Size Control of Open-Hearth Carbon Steel," TRANSACTIONS, American Society for Metals, Vol. 22, December, 1934, p. 942.

[7]H. W. McQuaid, E. W. Ehn, "Effect of Quality of Steel on Case-Carburizing Results," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol 67, 1922.

The Background of the Aluminum Addition

Before going too directly into the subject of aluminum and its importance to the steel user, it is well to divert our attention for the moment to those small developments from which arose the present interest in the subject of the aluminum addition.

Occasionally in days gone by, in checking case hardened parts by the routine case depth fracture test, direct-quenched pieces would be found that did not show the characteristic coarse crystalline fracture of the plain carbon steel being tested, but would show a fine case with a fine fibrous core fracture. When these appeared they were often analyzed and found to be of the usual analysis with no alloy present. No explanation could be found and these pieces were spoken of as having some peculiar characteristics which made them "perfect" or free from grain growth after long heating at 1700 degrees Fahr. (925 degrees Cent.). It was noted that case hardened parts from those heats which showed the so-called "perfect" fracture were tougher and gave some more trouble in hardening, but when most of the quenching was done in brine, little real trouble was experienced. When the quenching was changed to water, however, and when, during the war, the number of steel sources increased, the trouble with soft work increased greatly and indicated certain sources and certain heats as being particular offenders. When heats were kept separate through the heat treating department, this was a point easily established. It is interesting to note that as early as 1919 the men in charge of the heat treating were brought into the dark room to see on the ground glass screen the difference between heats which acted "normally" and those which acted "abnormally" as far as the production of satisfactory hardened cases was concerned. The characteristic difference between the coarse normal heats and the fine abnormal heats was obvious to the men directly in charge of the heat treating, and it became the practice to divert the fine-grained abnormal heats to other uses. Since they were the exception, this was no particular hardship. In checking among metallurgical aquaintances at that time, it was found that this difficulty of soft work in the plain carbon carburizing steel was not new, especially in the making of camshafts and piston pins. One automobile company kept on hand a supply of camshafts which had good hardening characteristics, and used these as a check against the steel source when they were in trouble—so that whatever the reason, the inability of a given lot of steel to produce good camshafts when the standard cam-

shafts were processing satisfactorily was considered sufficient cause for rejection.

It was soon found that the coarse-grained very normal type, while specifically good for high uniform hardness in case hardened, plain low carbon, water-quenched steel, was not suited to alloy gears and many other applications. This of course was due to the deeper hardening characteristics, the increased warpage and the decreased toughness which came with the coarse grain normal type. It was recognized as far back as 1922 that the finer grained types were better for gears and other alloy grades. Being in a position to compare steel in large quantities from various sources both in the plain carbon and alloy case hardening types, it was early recognized by your lecturer that the inherent characteristics of hardenability, toughness, etc., in these steels varied from mill to mill as well as from heat to heat. The difference in ductility, distortion, etc., was easily checked when making hundreds of thousands of duplicate parts of case hardened carbon steel in a form which permitted easy checking for ductility in the hardened condition.

It is interesting to remember the many interesting discussions of fifteen years ago, especially those concerning the use of aluminum. It was plainly evident by 1922 that the properties of case hardened steel were very much affected by the aluminum additions, and it was agreed then that for some applications the improved toughness made additions of aluminum very desirable. It was interesting at that time to compare the relative toughness of identical parts made from different heats and especially from different sources. The product was such, (bearing races) that crushing tests could easily be made to compare the amount of bend before fracture as well as the fracture, and hence many tests could be made from a given heat without difficulty. It was soon established that the so-called coarse-grained normal steel was very brittle as compared to the finer grained types, and the fracture much poorer when single quenched. Since the so-called less abnormal types of plain carbon steel could be apparently successfully hardened in the spray quench, then used, it was decided back in 1922 that the addition of a carefully regulated addition of aluminum to the properly killed heat was desirable to insure the best combination of toughness and hardness. Early in 1923 it was the opinion of one of our leading alloy steel makers that the coarse-grained normal steel was undesirable for gears because of increased distortion and low impacts. Even then it was noted that the coarse-

grained type would, with the normalizing equipment then available, give apparently better results in machining.

As noted before, as far back as 1922 the advisability of adding aluminum to heats to improve the "toughness" of the finished part was discussed. In fact, records available show one steel maker in 1919 adding over one pound of aluminum per ton in the ladle to commercial nickel-chromium steel to improve the "toughness."

Many cases could be cited where carefully regulated combinations of scrap, aluminum additions, etc., were made as far back as 1922. These additions were made to develop better impact values, better fractures, less distortion, etc., and aluminum up to three pounds per ton was used. Bearing steels, axle steel, and gear steels were subject to this control and the attention of the mill metallurgist was centered on the alloy grades rather than the carbon grades, although in certain cases such as in plain high carbon lock washer stock, etc., aluminum additions were made to improve the ability to distribute stresses and reduce cracking.

While much work was being done on the effect of grain-size from 1922 on, and the value of applying the new knowledge was soon recognized, the means for controlling and obtaining the different types were seldom discussed. The introduction of the first grain-size chart in 1924 was evidence that the very intensive study of the data obtained in investigating the effect of deoxidation methods on the characteristics of the finished steel was bearing fruit. It also indicated the value of the carburizing test as a means for indicating the characteristics to be expected in the steel as made.

It is interesting to read the discussion by M. H. Schmid of the original paper by Mr. Ehn and myself in which he indicates the extensive manner in which the carburizing test (McQuaid-Ehn) was applied in 1920-1921 at the plant of the United Alloy Steel Corporation to alloy steels. This work marked the first study of grain-size and normality as we know it today, and soon developed the connection between the grain-size and steel characteristics as well as the connection between deoxidation methods and steel characteristics, as witness the first grain-size chart of 1924.

Quoting from the discussion of Mr. Schmid[7] of the 1922 paper —"The method outlined . . . . offers opportunities of improvement in the product itself and in the selective application of that product. It offers an opportunity for constructive study and experimentation as to the most efficient methods of deoxidation, also for the selective

application of heats to meet specific conditions." In view of what has been done since then, this statement of Mr. Schmid was indeed prophetic.

In spite of the fact that from 1922 on, an intensive study was being made of grain-size, deoxidation and its relation to grain-size, and the relation of grain-size to results in the finished material, little if anything was published as to the methods employed in so-called grain-size control.

Due to customer and sales pressure, it became increasingly important that a mill producing special steels be fully familiar with the practical problems involved in producing steels having the grain-size (and characteristics) demanded by the steel user. From 1922 on, many investigations were made of the factors involved which affected the characteristics of the final product. These investigations covered every phase of steel-making from scrap to finished product, and particular emphasis was put on deoxidation control since it was soon learned that the most important factor in controlling the effect of the aluminum used was in the degree of oxidation and the type of oxides present when the deoxidizers were added. During the development of the practical side of steel-making to definite characteristics, much was being done to educate the user on the importance of factors other than chemistry and soundness in the relation of a steel specification to meet a certain part.

In all this work the importance of the part played by aluminum was kept very much in the background. It is only natural that the electric furnace steel maker, who had a more stable and uniform condition of oxidation in the finished steel, should be able to obtain control of the aluminum effect before the open-hearth man could. In fact, for a time, this easier control of uniformity of oxidation and aluminum effects gave the large electric steel maker a definite advantage, and this advantage resulted in a considerable encroachment of electric furnace alloy steel in the field of the basic open-hearth. See Hardy.[2]

With the proper customer pressure developed, however, the open-hearth special steel producer was forced to develop the necessary technique to produce steels of the characteristics demanded by the user, with the result that we are just emerging into a new understanding of the possibilities of the basic open-hearth furnace as a producer of high grade steel.

One of the reasons for keeping the part played by aluminum

more or less a secret was the old prejudice against aluminum, due to its use in the past to quiet "wild" heats, etc. There had also been circulated considerable publicity as to the disastrous effects of visible alumina inclusions on soundness, machinability and other requirements for good steel. These effects were, of course, ascribed to aluminum as a deoxidizer and they were due primarily to a lack of knowledge of how a heat of steel should be prepared before an extremely active deoxidizer such as aluminum is added.

There is little, if any evidence that the correct addition of a fairly large amount of aluminum to a properly prepared heat will increase to an unsatisfactory extent the amount of visible nonmetallic inclusions. It cannot be denied that there is some tendency to an increase in the number of inclusions rated as oxides with an increase in aluminum, but the effect on the number of so-called "slag" inclusions is nil.

The increase in the oxide inclusion rating is at the worst small and affected by other variables than aluminum, such as temperature, rate of and extent of deoxidation, etc.

Epstein[6] states that aluminum either in the ladle or in the mold does not necessarily result in an increase in inclusions. In plotting inclusion ratings against aluminum additions, it was found that the low aluminum heats killed with manganese and silicon were lowest in oxide-type inclusions, while the low manganese, low silicon heats with aluminum were the highest that could be expected.

Investigating the Aluminum Addition

Much work has been done to determine the balance between the condition of the steel to which the aluminum is added, the timing of the addition in relation to the time of solidification, and the size of the addition. This work, however, has been on a large scale, involving commercial heats, and the results have been more or less empirical.

In the effort to determine more accurately the effect of aluminum additions to plain carbon steel of varying carbon and manganese contents, steel was made in a 300-pound Moore 'Lectromelt furnace using the same base scrap in every case as well as the same (prepared) slag.

The total metallic charge used was cut from sheet bar all from the same ingot of a low carbon rimmed steel heat of the following analysis, per cent:

C	Mn	Si	P	S	N	Al	Al_2O_3	Cu	Ni	Cr
0.05	0.05	0.04	0.010	0.030	0.040	0.019	0.010	0.05	0.02	0.02

This steel was melted in a basic open-hearth furnace under a finishing slag which analyzed as follows, per cent:

FeO	Fe_2O_3	MnO	SiO_2	CaO	MgO	P_2O_5	Al_2O_3	S
27.5	10.2	10.6	9.8	31.8	6.4	2.0	1.68	0.13

Aluminum addition in ladle was eight ounces per gross ton, the heat rimming well and nothing in any way being unusual.

From this standard charge, fourteen heats were made under as uniform conditions as possible, each heat making three ingots. Each ingot was poured from a separate hand ladle and the aluminum was added to the ladle. The aluminum was wired to a rod and plunged rapidly into the clean surface of the steel in the ladle after making an opening in the slag. The molds were poured immediately thereafter. (For complete analysis see Table I.)

The ingots were heated and rolled by hand on a standard 18-inch rolling mill to 1½-inch diameter bars, a record being kept of rolling temperatures, etc. These bars were sampled for "as-rolled" test pieces, and then normalized at 1800 degrees Fahr. (985 degrees Cent.) for one hour.

Studies were made of samples from each heat in the as-rolled, normalized and heat treated condition. These studies included grain growth, grain-size, normality, hardenability, impact values, etc., as shown in the following discussion of the results.

It should be admitted at this point that while we have no difficulty in obtaining close chemical analysis checks on the usual elements found in steel, it has been found that the determination of metallic aluminum and alumina offers considerable field for discussion. Several methods were tried in an effort to get consistent results and the method developed by our Central-Alloy laboratory did show excellent checks when very carefully followed. It was found that the analyzed aluminum did not check too closely with the aluminum additions, but it was evident that the difference between the analyzed and added aluminum indicated a loss and that the loss increased from the first to last ingot.

The metallic aluminum as analyzed is not assumed to be closely accurate in spite of the rather good checks obtained, but it is considered as indicative of the metallic aluminum content and for the purpose of this investigation satisfactory. Work is being done at

Table I

Chemical Analysis of Experimental Heats

Group I

Heat No.	C	Mn	Si	P	S	Al	Al_2O_3	Ni
024	0.40	0.91	0.12	0.012	0.019	0.012	0.019	0.0140
522	0.40	0.95	0.15	0.011	0.030	0.032	0.030	0.0137
122	0.40	0.88	0.18	0.014	0.020	0.026	0.028	0.0142
222	0.37	0.70	0.17	0.013	0.022	0.098	0.020	0.0068
323	0.36	0.74	0.15	0.013	0.028	0.117	0.026	0.0068
422	0.37	0.72	0.17	0.020	0.025	0.204	0.023	0.0074

Group II

Heat No.	C	Mn	Si	P	S	Al	Al_2O_3	Ni
022	0.335	0.45	0.16	0.011	0.029	0.017	0.022	0.0135
521	0.33	0.44	0.19	0.014	0.023	0.013	0.027	0.0097
121	0.325	0.39	0.20	0.019	0.027	0.016	0.026	0.0091
221	0.38	0.44	0.12	0.016	0.023	0.015	0.044	0.0137
322	0.37	0.44	0.15	0.009	0.028	0.055	0.040	0.0132
411	0.26	0.41	0.09	0.009	0.020	0.173	0.029	0.0142
212	0.26	0.49	0.17	0.006	0.022	0.120	0.053	0.0124
421	0.35	0.40	0.15	0.015	0.028	0.129	0.037	0.0115
312	0.26	0.42	0.17	0.020	0.020	0.156	0.034	0.0153

Group III

Heat No.	C	Mn	Si	P	S	Al	Al_2O_3	Ni
015	0.245	1.05	0.14	0.022	0.027	0.011	0.013	0.0111
115	0.245	0.94	0.23	0.011	0.024	0.032	0.022	0.0110
014	0.262	1.01	0.14	0.017	0.021	0.018	0.024	0.0190
513	0.27	1.10	0.19	0.014	0.023	0.024	0.027	0.0196
116	0.26	1.00	0.14	0.013	0.027	0.024	0.016	0.0196
413	0.26	0.95	0.25	0.010	0.025	0.156	0.060	0.0104

Group IV

Heat No.	C	Mn	Si	P	S	Al	Al_2O_3	Ni
118	0.25	1.14	0.18	0.023	0.070	0.024	0.012	0.0185
117	0.24	1.03	0.20	0.020	0.090	0.038	0.025	0.0091
114	0.26	0.89	0.15	0.012	0.125	0.048	0.032	0.0089

Group V

Heat No.	C	Mn	Si	P	S	Al	Al_2O_3	Ni
223	0.49	1.49	0.18	0.012	0.023	0.130	0.035	0.0146
324	0.49	1.44	0.18	0.013	0.026	0.124	0.054	0.0144
423	0.49	1.41	0.25	0.012	0.024	0.046	0.050	0.0121

Group VI

Heat No.	C	Mn	Si	P	S	Al	Al_2O_3	Ni
021	0.39	0.82	0.15	0.023	0.025	0.012	0.022	0.0123
523	0.38	0.85	0.13	0.015	0.028	0.011	0.020	0.0115
123	0.39	0.80	0.15	0.023	0.028	0.015	0.013	0.0111

Group VII

Heat No.	C	Mn	Si	P	S	Al	Al_2O_3	Ni
213	0.12	0.54	0.10	0.012	0.024	0.020	0.044	0.0114
412	0.12	0.51	0.16	0.009	0.025	0.047	0.024	0.0128
313	0.12	0.46	0.26	0.012	0.022	0.110	0.045	0.0119
111	0.16	0.18	0.03	0.006	0.021	0.019	0.035	0.0107
211	0.19	0.22	0.02	0.012	0.024	0.014	0.044	0.0115
321	0.32	0.26	0.03	0.006	0.023	0.120	0.025	0.0190
013	0.21	0.76	0.19	0.022	0.022	0.035	0.006	0.0124
512	0.204	0.64	0.18	0.012	0.025	0.046	0.030	0.0114
113	0.21	0.54	0.17	0.022	0.022	0.017	0.013	0.0120
012	0.20	0.39	0.15	0.010	0.026	0.014	0.018	0.0107
311	0.19	0.33	0.18	0.008	0.028	0.048	0.048	0.0111
023	0.32	0.29	0.17	0.018	0.026	0.017	0.012	0.0059

this time in conjunction with the Aluminum Company of America to develop more accurate and rapid methods and it is believed that in a short time a practical accurate method of determining aluminum will be available.

In considering the results which might be deduced from the data available, we should perhaps review some of the prevailing views which have been advanced as to the causes of the variation in the characteristics of the finished steel.

Bain in his Campbell Memorial Lecture in 1932, gives an exceedingly clear-cut exposition of the connection between effective grain-size and the austenite transformation rate which governs the inherent hardenability of a given steel. The fine grain is dependent

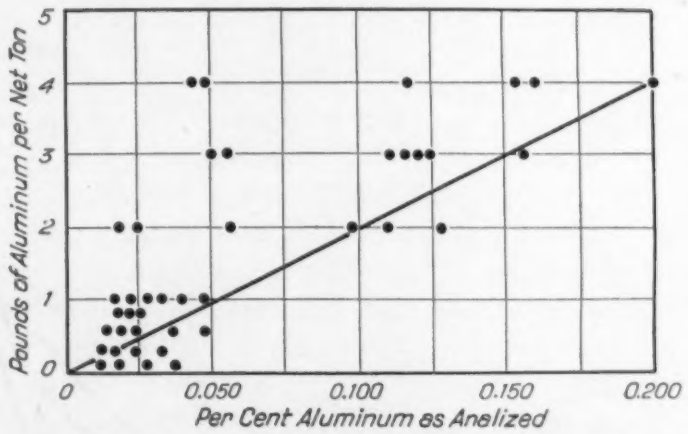


Fig. 2—Aluminum Added, as Compared with Aluminum as Analyzed. The Straight Line Indicates Theoretical Addition.

on, he suggests, the obstruction to grain growth by large numbers of very finely dispersed particles comprised presumably of stable oxides of alumina, vanadia, etc.

He suggests that metallic aluminum as an alloy in steel acts to promote normality and contributes to shallow hardening, its effect as a grain growth inhibitor being due to dispersed insoluble alumina particles.

Epstein and Rawdon[1] in their very complete report of an extensive investigation of steels of case hardening grade, report that aluminum added to the mold (as well as vanadium) promotes fine grain, abnormal structure, and affects thereby the inherent hardenability characteristics of the steel to which it is added.

Hardy[2] was one of the first to point out the advantages of grain-size control and particularly the relation between grain-size and

toughness in quenched steels. He did not indicate how the control of the grain-size was obtained, although he was one of the pioneers in this field and made a thorough study of the effect of aluminum additions to electric furnace steel.

Herty, Larsen[8] et al indicate manganese content as a primary factor in affecting normality and the importance of aluminum additions. It has been stated that high manganese steels are of uniformly high hardenability while the low manganese steels are of low hardenability and that manganese is a primary requisite for deep hardening steels without other alloy.

Scott[9] on experimental melts showed that the impact values in steels low in oxygen are directly affected by the aluminum content.

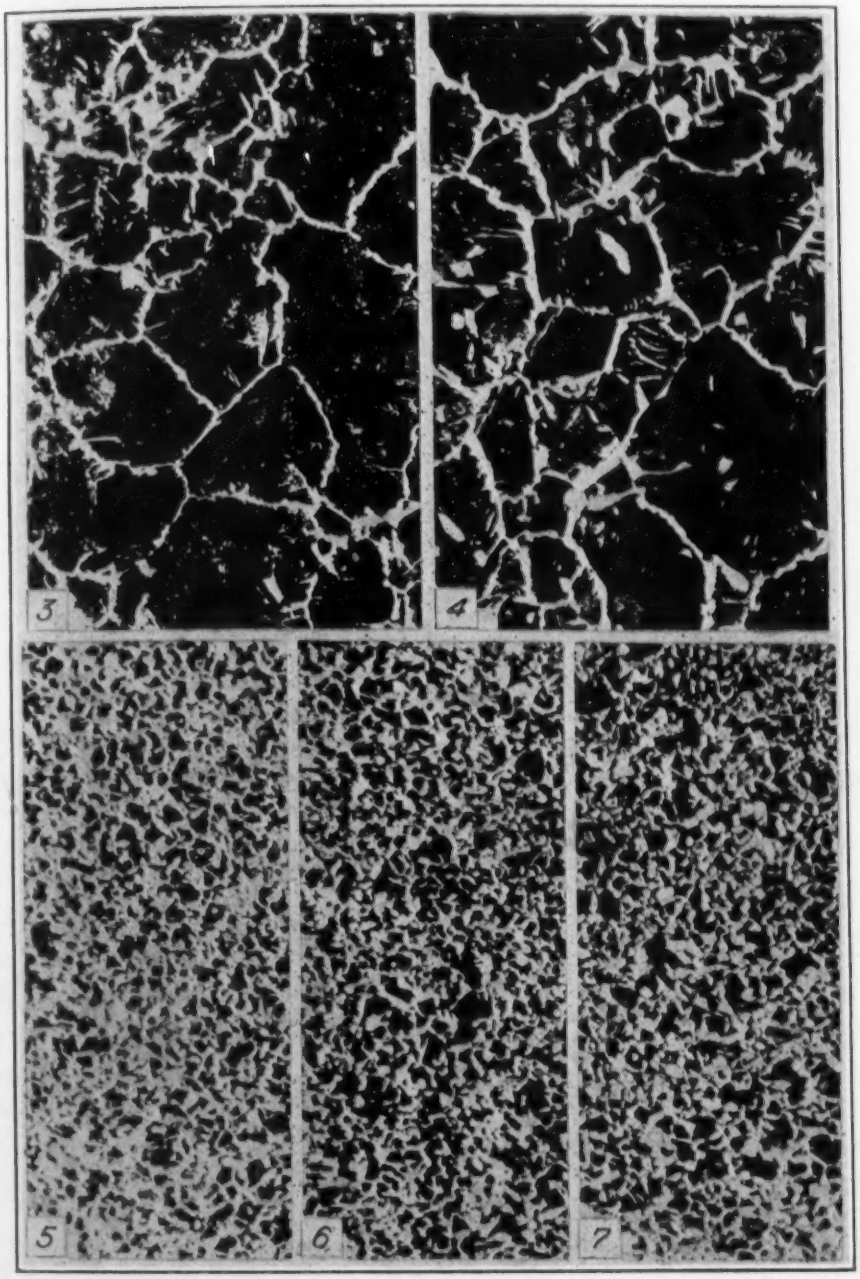
Many have been the corroborating tests, particularly in practice to indicate the advantage of controlled hardenability, and it is not necessary to restate at this point the reason for grain-size control. Thus we might sum up the importance of what is termed "grain-size" control by stating that this variation in "grain-size" is one of the most important factors, if not the most important factor in determining the reason for the variation in response to quenching, the response to normalizing, and the inherent toughness which exists in commercial heats of steel in spite of close control of chemistry, or at least the usual chemistry. This variation in properties is of tremendous importance to the user of steel and hence warrants our best efforts to determine the part played by such a factor as aluminum, which is our main reliance today.

As an example of the variation which could be expected from heats of approximately the same analysis except for variations in aluminum addition, we can look at microstructures of normalized bars of this material.

Figs. 3 to 7 showing heats 523, 123, 222, 323 and 422, illustrate the very coarse structure of bars normalized for one hour at 1800 degrees Fahr. (985 degrees Cent.) and cooled in air when the aluminum content is low and the entirely different looking and much finer structure of bars from heats of practically the same analysis but with a fairly high percentage of aluminum when treated the same way. The same difference in structure occurs in the as-rolled bars providing the finishing temperatures are not high enough

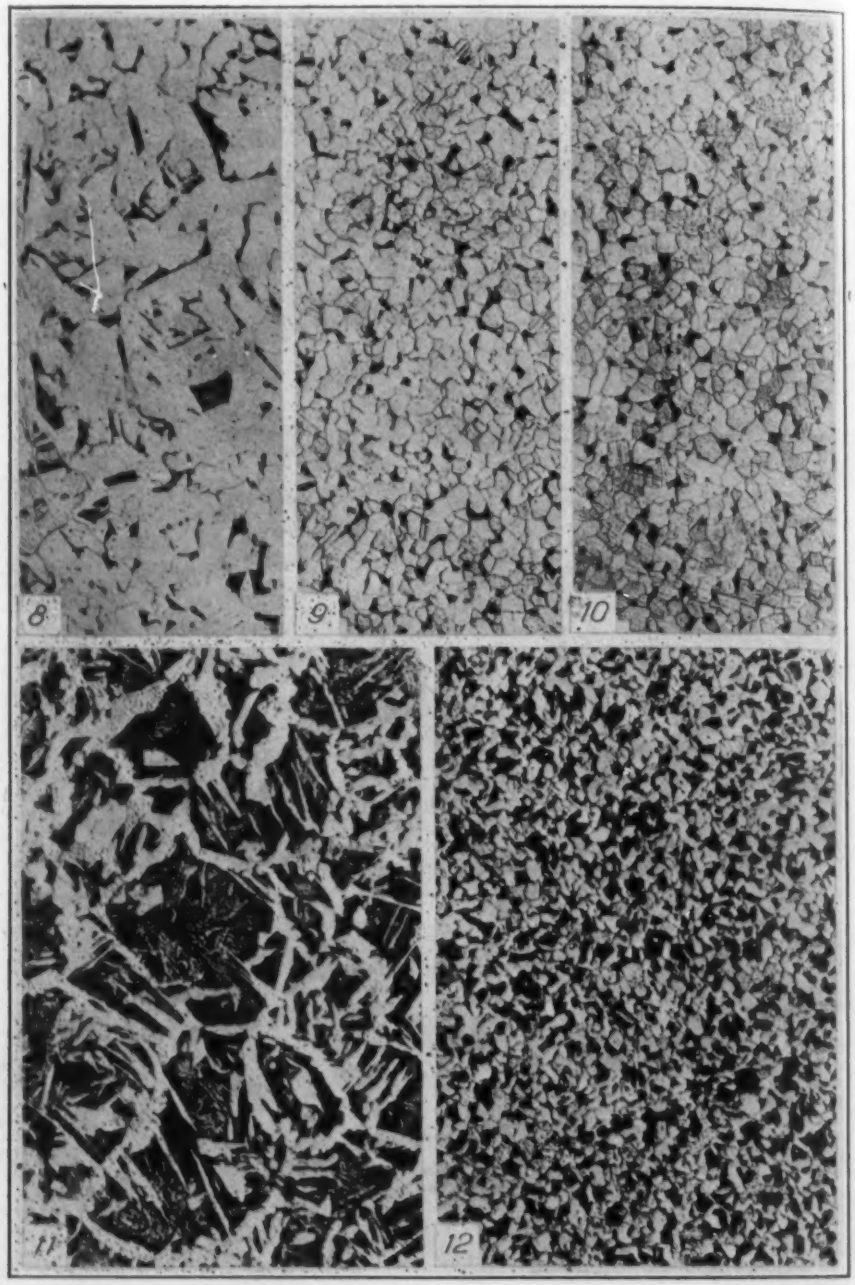
[8]C. H. Herty, Jr., B. M. Larsen, et al, "Abnormality in Case Carburized Steels," Mining and Metallurgy Cooperative Bulletin No. 45, Pittsburgh, 1929.

[9]Howard Scott, "Factors Determining the Impact Resistance of Hardened Carbon Steels," TRANSACTIONS, American Society for Metals, Vol. 22, December, 1934, p. 1142.



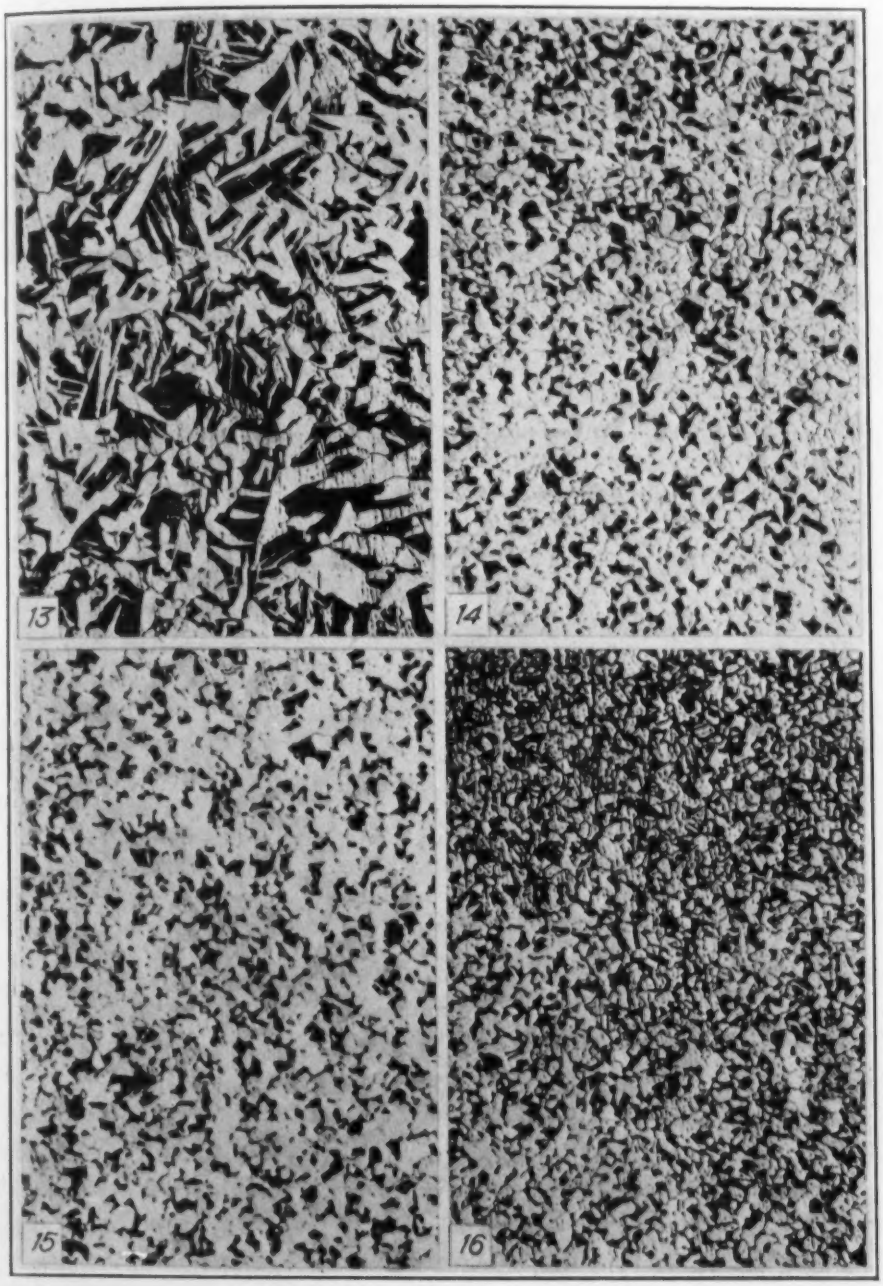
Figs. 3 to 7—Microstructure of Heats 523, 123, 222, 323 and 422 Respectively. Bars Normalized for 1 Hour at 1800 Degrees Fahr. (985 Degrees Cent.). Cooled in Air. × 100.

to coarsen the structure of the heats to which aluminum has been added, which is quite often the case in smaller sizes of bars. This difference in structure is of importance in cold shearing, tendency to form seams, etc.



Figs. 8 to 12—Microstructure of Heats 213, 412, 313, 221 and 322 Respectively. Bars Normalized for 1 Hour at 1800 Degrees Fahr. (985 Degrees Cent.) Cooled in Air. × 100.

Figs. 8 to 12 of heats 213, 412, 313, 221 and 322 show the same variation in structure after normalizing as the heats given before, indicating that the aluminum added has a definite effect on the normalized and as-rolled structure.



Figs. 13 to 16—Microstructure of Heats 121, 212, 312 and 411 Respectively. Bars Normalized for 1 Hour at 1800 Degrees Fahr. (985 Degrees Cent.). Cooled in Air. × 100.

Figs. 13 to 16 of heats 121, 212, 312 and 411 show a similar variation. It is quite evident from a casual study of these normalized structures that the steel user is very definitely interested in the addition of aluminum to the steels which he uses.

If these same heats are carburized according to the standard A.S.T.M. procedure for grain-size using temperatures of 1800 degrees Fahr. (985 degrees Cent.) and 1900 degrees Fahr. (1040 degrees Cent.), as well as 1700 degrees Fahr. (925 degrees Cent.), it will be found that there is a definite relation of grain-size and grain growth to the aluminum additions, indicating that directly or indirectly the aluminum is related to not only the grain-size at 1700 degrees Fahr. (925 degrees Cent.), but the grain growth at higher temperatures, a fact which has been very well shown by Epstein, Herty, etc.

Table II

A.S.T.M. Grain-Size After Carburizing 8 Hours at Temperatures Given

Heat	C	Mn	Si	Al	Degrees Fahr. 1700	1800	1900	
523	0.38	0.85	0.13	0.011	2	2	2	Normal
123	0.39	0.80	0.15	0.015	2	2	2	Normal
222	0.37	0.70	0.17	0.098	6	6	6	Abnormal
323	0.36	0.74	0.15	0.117	6	6	6	Abnormal
422	0.37	0.72	0.17	0.204	7	7	7	Abnormal
213	0.12	0.54	0.10	0.020	2	2	2	Normal
412	0.12	0.51	0.16	0.047	6	3	2	Abnormal to 1900° Fahr.
313	0.12	0.46	0.26	0.110	7	7	6	Abnormal
221	0.38	0.44	0.12	0.015	2	2	2	Normal
322	0.37	0.44	0.15	0.055	7	6	2	Abnormal to 1900° Fahr.
121	0.33	0.39	0.20	0.016	2	2	2	Normal
212	0.26	0.49	0.17	0.120	7	7	7	Abnormal
312	0.26	0.42	0.17	0.156	7	7	7	Abnormal
411	0.26	0.41	0.09	0.173	7	7	7	Abnormal

Now if fracture tests are made on these same heats according to the method developed by Shepherd,[10] we find that there is also a relation between the aluminum addition and the fracture appearance. If we study Table II, it will be found that there is a tendency toward increasingly fine fracture with increasing aluminum, especially at 1700 degrees Fahr. (925 degrees Cent.). This would indicate a relation between the McQuaid-Ehn grain-size and the Shepherd fracture standard, although this agreement, especially at 1900 degrees Fahr. (1035 degrees Cent.) is not quite as close as we might expect, and indicates that the McQuaid-Ehn grain-size differs somewhat from the Shepherd test probably due to the fact that the McQuaid-Ehn grain-size depends upon the formation of excess carbide which tends to inhibit the grain growth at a higher temperature than

[10]B. F. Shepherd, "The P-F Charactertistic of Steel," TRANSACTIONS, American Society for Metals, Vol. 22, December, 1934, p. 979.

would be the case in the uncarburized test pieces used in the Shepherd test.

An effort was made to establish a direct connection between the so-called toughness value in both the normalized and heat treated condition and the aluminum as analyzed. In most cases it was found that the Izod value was directly related to the hardness which in turn was related to the grain-size, a fact which has been well estab-

Table III
Fracture Grain-Size (Shepherd Standard) Showing Effect of Aluminum

Heat	C	Mn	Si	Al	Degrees Fahr. 1400	1500	1600	1700	1800	1900
523	0.38	0.85	0.13	0.011	4¾	5	3¼	2¼	2	2
123	0.39	0.80	0.15	0.015	6	5	5¼	1	1	1
222	0.37	0.70	0.17	0.098	5¾	6¾		6	6	2
323	0.36	0.74	0.15	0.117	5¼	6	5¾	5½	5½	2
422	0.37	0.72	0.17	0.204	4¾	7	5¾	5¾	1	1
213	0.12	0.54	0.10	0.020	2¼	3½	4	2	2	1
412	0.12	0.51	0.16	0.047	4	4	5	4	2	1
313	0.12	0.46	0.26	0.110	3¾	4	4	7	6	1
221	0.38	0.44	0.12	0.015	3¼	5½	1¼	1¼	1¼	1
322	0.37	0.44	0.15	0.055	4¾	5¾	5	6	5½	1
121	0.33	0.39	0.20	0.016	3¼	5¼	1½	1½	1	1
212	0.26	0.49	0.17	0.120	3¾	6	5½	4½	4	2
312	0.26	0.42	0.17	0.156	4	6	4½	5½	1	1
411	0.26	0.41	0.09	0.173	4	7	5	5	5	1

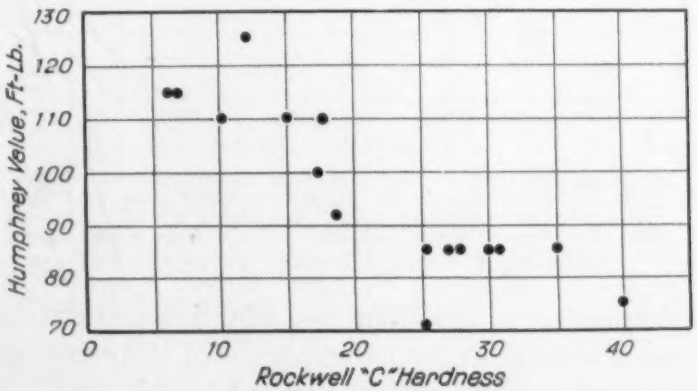


Fig. 17—Showing Relation Between Humphrey Value and Depth Hardness. Humphrey Value from Notched Izod Test Pieces Directly Quenched After Carburizing at 1700 Degrees Fahr. for Four Hours. Rockwell C Value from Depth Hardness Checks on 1-Inch Rods Quenched in Water from 1700 Degrees Fahr.

lished by others. In the carburized and hardened specimens, as well as the heat treated specimen, the Izod tests are not sufficiently sensitive to indicate a direct relation with the aluminum as added, except to show that the higher Izod values were obtained in higher aluminum fine grain heats and varied closely with the hardness obtained.

In an effort to check the toughness of the carburized case, tests were made to determine the Humphrey deflection values on carburized test pieces from the low carbon heats. This test consists of a slow bend given to a standard Izod test piece in which it is possible to measure not only the foot pounds required to produce failure, but also the deflection which occurs, due to the application of the load.

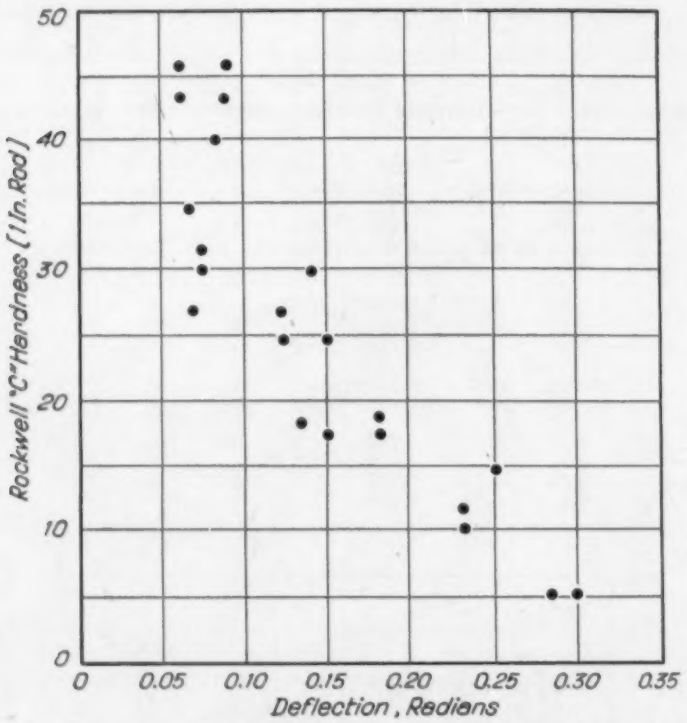


Fig. 17A—Showing Relation Between Humphrey Deflection Value and Depth Hardness. Humphrey Value from Izod Test Pieces Directly Quenched After Carburizing at 1700 Degrees Fahr. for Four Hours. Rockwell C Value from Depth Hardness Checks 1-Inch Round 1700 Degrees Fahr. in Water.

It is interesting to note that the deflection and the foot pounds applied bear a relation to the hardenability of the steel used in making a carburized test piece, and that while this test indicates the ability of the carburized and hardened case to deflect before cracking, the hardenability characteristic of the heat is an important factor in the result. While there was not much variation in the hardness of the Humphrey test piece itself, due to the small size and severe quench, it would seem that the general hardenability characteristic of the heat which in turn is related to the aluminum addition has a direct bearing on the toughness of a carburized case and hence the user of case hardened material which is of such great im-

portance in the manufacture of gears, etc., is again much interested in the addition of aluminum to the heats of steel with which he is furnished.

Fig. 18 shows the relation between the hardness at the center of a 1-inch section quenched from 1700 degrees Fahr. (925 degrees Cent.) in water and the aluminum as analyzed. These heats were

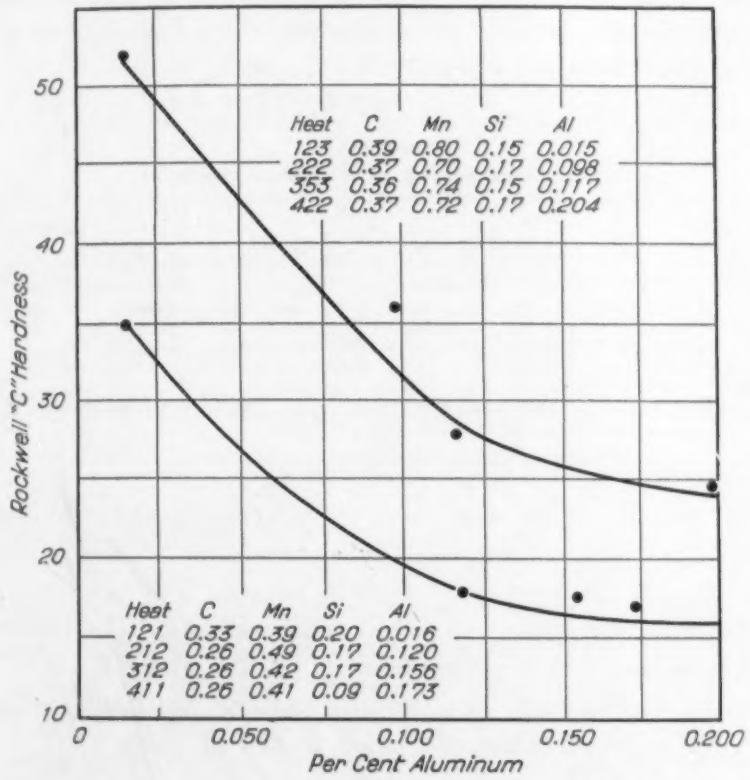


Fig. 18—Showing the Relation Between Hardenability of 1-Inch Diameter Section Quenched from 1700 Degrees Fahr. in Water and Aluminum as Analyzed.

selected because of their close carbon, manganese and silicon range, and results indicate a definite relation between the depth of hardness and the aluminum addition. It could, of course, be shown that there is a relation between the grain-size and the depth of hardness —a relation which is well known due to the work of Bain and Davenport. It can also be shown, of course, that there is a relation between grain-size and aluminum addition so that all we can state is, that apparently the aluminum bears a definite relation to the grain-size in the heats in question, as well as to the hardenability, and that whether the hardenability characteristic is due directly to the fine

grain or aluminum addition is difficult to determine with our present knowledge, and might be the subject for a rather interesting discussion and investigation.

Statements have been made to the effect that manganese has an important relation to normality, grain-size, hardenability, etc. Let us see if we can assemble, from the data available, any information which will indicate how important manganese is in this respect. As an example, let us see now what are the characteristics of the low manganese, low aluminum heats. See Table IV.

Table IV
Low Manganese—Low Aluminum Steels

Heat No.	C	Mn	Si	Al	Normalized Micro-Structure	McQuaid-Ehn Grain Size	Shepherd Fracture	Rockwell C. Center 1" Diam. as Quenched
111	0.16	0.18	0.03	0.019	Coarse	Coarse and	Coarse	20
221	0.38	0.44	0.12	0.016	Coarse	Normal — to	all	37
012	0.20	0.39	0.15	0.014	Coarse	1900 degrees Fahr.	temp.	25

Remarks

McQuaid-Ehn taken at 1600-1700-1800-1900 degrees Fahr. Rockwell test Quenched from 1700 degrees Fahr. in water.

Here we see steels that are all coarse-grained by both the McQuaid-Ehn test and as actually normalized. These heats are very normal and show no grain growth because they are very coarse by the Shepherd standard even at low temperatures. The hardness in the quenched condition is good for steel of this analysis.

Now let us examine some low manganese heats with a definite addition of aluminum, taking the heats shown in Table V.

Table V
Low Manganese Heats with Added Aluminum

Heat No.	C	Mn	Si	Al	Normalized Micro-Structure	McQuaid-Ehn Grain-Size	Shepherd Fracture	Rockwell C. Center 1" Diam. as Quenched
321	0.32	0.26	0.03	0.120	Fine	Fine — Abnor-	Fine to 1900 degrees Fahr.	17
312	0.26	0.42	0.17	0.156	Fine	mal to 1900	Fine to 1800 degrees Fahr.	17
411	0.26	0.41	0.09	0.173	Fine	degrees Fahr.	Fine to 1900 degrees Fahr.	16
212	0.26	0.49	0.17	0.120	Fine		Fine to 1800 degrees Fahr.	17

Here we have an entirely different set of results. Normalized structures are fine-grained and the carburizing test also shows a fine structure even after carburizing for 8 hours at 1900 degrees Fahr. (1035 degrees Cent.), and the hypereutectoid zone is definitely ab-

normal. The grain growth fracture test of Shepherd's shows relatively little growth to 1900 degrees Fahr. (1035 degrees Cent.) and the hardness readings are markedly lower than the heats previously examined. We can hardly explain this difference in characteristics by variation in carbon or manganese. If we neglect the aluminum content, it is difficult to explain the difference between these two groups, so, until something better shows up we will credit the difference to the aluminum addition.

Now let us take some high manganese heats with low aluminum content and see what the characteristics of this group are. (Table VI)

Table VI
High Manganese Heats with no Aluminum Addition

Heat No.	C	Mn	Si	Al	Normalized Micro-Structure	McQuaid-Ehn Grain-Size	Shepherd Fracture	Rockwell C. Center 1" Diam. as Quenched	Remarks
014	0.26	1.01	0.14	0.018	Coarse	Coarse and Normal to 1900 degrees Fahr.	Coarse to 1900 degrees Fahr.	45 46	Shepherd test somewhat finer Below 1700 degrees Fahr.
513	0.27	1.10	0.19	0.024	Coarse				

Here we have once more, coarse-grained normalized structures, with the grain-size after carburizing showing a coarse hypereutectoid zone with a normal cementite boundary. Apparently the addition of manganese to the first group examined does not change markedly the characteristics of the steel, although the hardening effect of the increased manganese is naturally noticeable. The Shepherd fracture grain growth test shows these heats to be on the coarse side up to 1700 degrees Fahr. (925 degrees Cent.) and definitely coarse above this temperature.

Supposing now we compare some high manganese heats to which aluminum has been added, such as those of Table VII.

Table VII
High Manganese Heats with Added Aluminum

Heat No.	C	Mn	Si	Al	Normalized Micro-Structure	McQuaid-Ehn Grain-Size	Shepherd Fracture	Rockwell C. Center 1" Diam. as Quenched
413	0.26	0.95	0.25	0.156	Fine	Fine to 1900 degrees Fahr.	Fine	23
323	0.36	0.74	0.15	0.117	Fine	Abnormal	to 1900	30
223	0.49	1.49	0.18	0.130	Fine	Abnormal	degrees	57
324	0.49	1.44	0.18	0.124	Fine	Abnormal	Fahr.	58

These heats are interesting in that they show a fine grain structure both in the normalized and carburized condition and they are of the abnormal type in spite of the high manganese content. These results would indicate that manganese in itself it really of minor importance when we are interested in grain control, response to normalizing, etc. It would seem from a study of these heats examined,

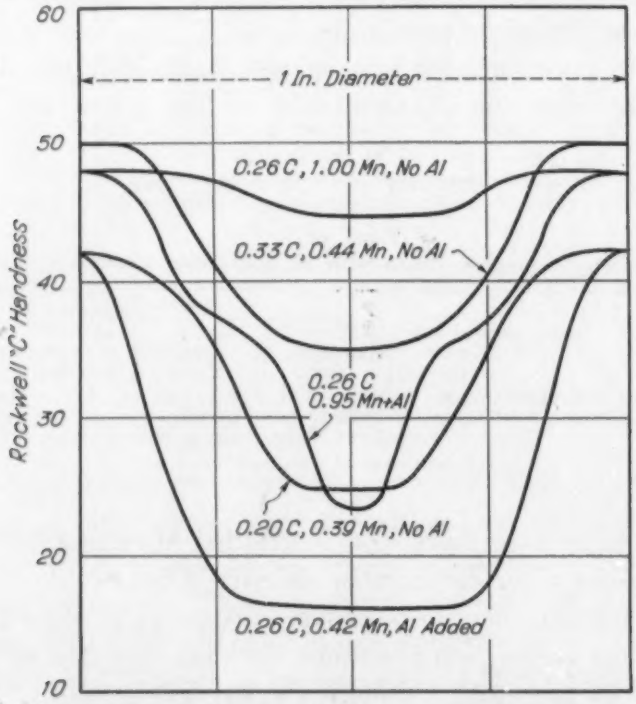


Fig. 19—Showing the Effects of Manganese and Aluminum Additions on the Hardenability of a 0.26 Per Cent Carbon Steel Water Quenched in 1-Inch Diameter Section from 1700 degrees Fahr. Note that 0.20 Per Cent Carbon, 0.39 Per Cent Manganese Without Aluminum Hardens Deeper Than 0.26 Per Cent Carbon, 0.42 Per Cent Manganese Plus Aluminum. Also that 0.33 Per Cent Carbon, 0.44 Per Cent Manganese Without Aluminum Hardens Deeper Than 0.26 Per Cent Carbon, 0.95 Per Cent Manganese with Added Aluminum.

that small additions of aluminum have marked effects on those characteristics of a heat of steel which are so important in controlling the heat treated properties of the finished part. This, of course, is not offered as anything new, since it is exactly for these things that we have been adding aluminum to steel to govern its characteristics after heat treatment for more than ten years. These results are given simply to show how much more important aluminum is in this respect than manganese.

It is interesting to compare the relative importance of aluminum

additions and manganese additions on the hardenability of plain carbon steels and now we will look at depth hardness curves made by quenching 1-inch diameter round pieces in water at 1700 degrees Fahr. (925 degrees Cent.) and measuring the hardness at different depths by means of Rockwell hardness testing.

Fig. 19 shows the effects of manganese and aluminum additions

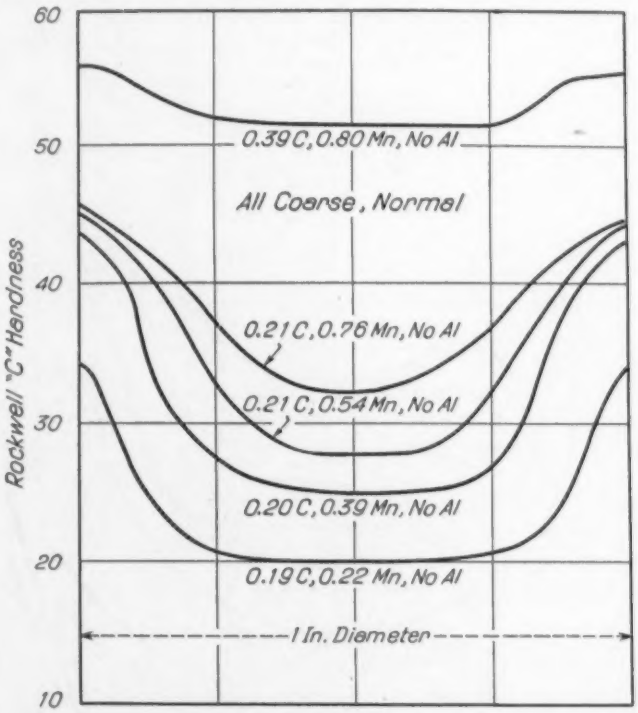


Fig. 20—Showing the Effect of Increasing Manganese on 0.20 Per Cent Carbon Steel Without Aluminum Addition, when Quenched in 1-Inch Section in Water from 1700 Degrees Fahr. Note the Comparative Hardness of a 0.39 Per Cent Carbon, 0.80 Per Cent Manganese Steel, Indicating the Relative Value of Carbon and Manganese in Improving Hardness Penetration.

on the hardenability of a 0.25 per cent carbon steel, water-quenched in 1-inch diameter sections from 1700 degrees Fahr. (925 degrees Cent.). Note that the 0.20 per cent carbon, 0.39 per cent manganese without the aluminum, hardens deeper than the 0.26 per cent carbon, 0.42 per cent manganese with aluminum. Note also that the 0.33 per cent carbon, 0.44 per cent manganese steel without aluminum hardens deeper than the 0.26 per cent carbon, 0.95 per cent manganese steel to which aluminum has been added.

Let us examine Fig. 20 showing the effect of increasing manganese on the hardenability of 0.20 per cent carbon steel without the

aluminum addition when quenched in 1-inch sections in water at 1700 degrees Fahr. (925 degrees Cent.). Note the comparative hardness of 0.39 per cent carbon, 0.80 per cent manganese steel without aluminum, indicating the relative value of carbon and manganese in improving hardness penetration.

Now let us take another series of steels of approximately the

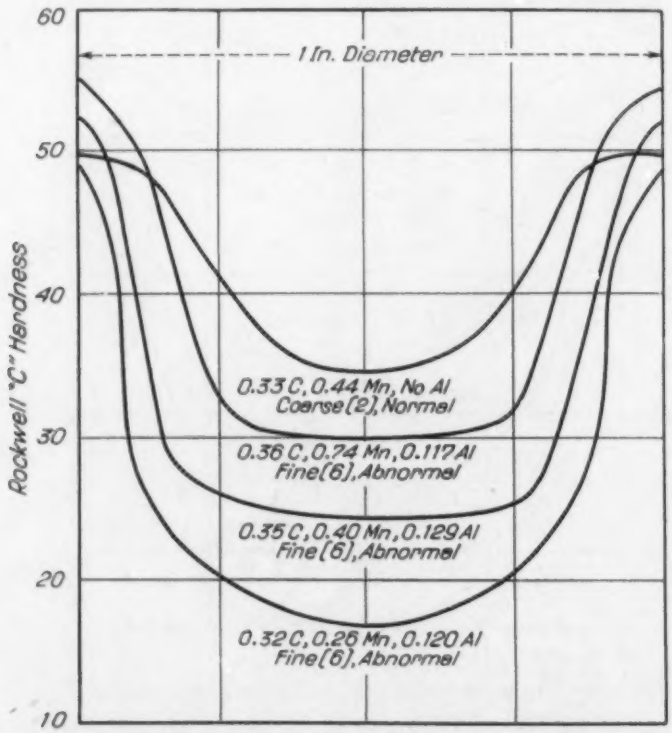


Fig. 21—Effect of Increasing Manganese on a Medium Carbon Steel Containing Relatively Heavy Additions of Aluminum, when Quenched in 1-Inch Diameter Section in Water, from 1700 Degrees Fahr. Note Effect of Aluminum, Indicating Relative Effects of Manganese and Aluminum on Hardness Penetration.

same carbon content but varying in manganese content and containing added aluminum, Fig. 21. Note the result of adding aluminum, indicating the relative effects of manganese and aluminum on hardness penetration. Compare the steel without aluminum with the other three steels to which aluminum has been added, showing in this case that the steel with considerably less manganese and without added aluminum will harden comparatively better.

The comparative effect of aluminum as added, on the hardenability of steels of approximately the same manganese and carbon

content is shown in Fig. 22. While, as discussed before, there is always some doubt as to the absolute accuracy of aluminum analysis, these heats selected according to increase in aluminum indicate that the hardenability decreases with increasing aluminum and perhaps according to some definite law. We could spend considerable time in discussing the curves shown because of their very valuable prac-

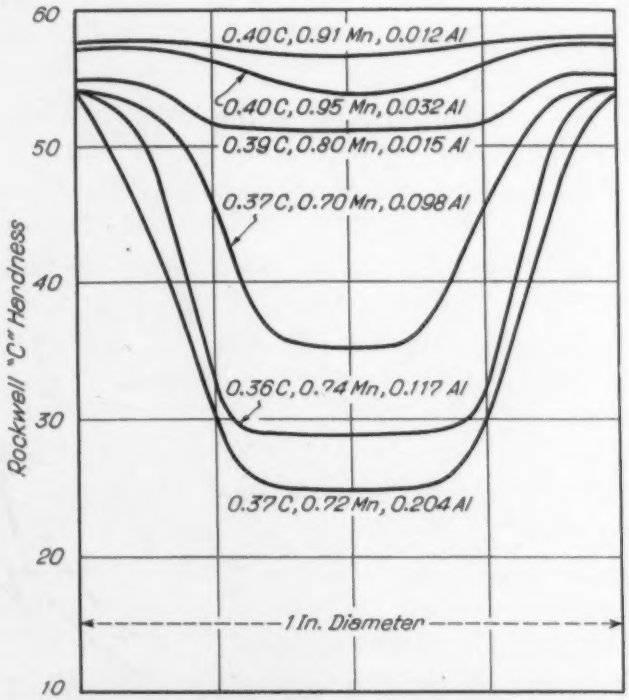


Fig. 22—Showing the Effect of Increasing Aluminum Addition on Hardenability of Medium Carbon, Manganese Steel Quenched in 1-Inch Section from 1700 Degrees Fahr. in Water. Aluminum Values are Metallic Aluminum as Analyzed.

tical application. Steel of the analysis given is used in great quantities in the heat treated condition and very often for applications of difficult design in which the hardening characteristics are closely related to internal stresses developed in quenching sections of non-uniform thickness.

Several interesting results from practice could be given where steels of this analysis have been found entirely unsuited for the parts for which they have been specified, due to being too deep hardening and thus tending to crack in quenching. In fact suitability of this steel for most purposes depends entirely on the ability to produce this analysis to a controlled hardenability requirement.

The Action of the Aluminum Addition

We have just shown some results indicating the connection between the aluminum addition, hardenability, grain-size, grain growth, etc. We might at this stage speculate on the reason for this connection. As stated before, it is generally assumed by the leading American metallurgists that the effect of aluminum is indirectly through submicroscopic particles of aluminum oxide which act as obstructing agents to grain growth and so produce the fine grain steels with all the accompanying characteristics. There are among us a few, however, who do not entirely subscribe to this explanation of the effect of the aluminum addition.

It cannot be denied that submicroscopic dispersion of infusible aluminum particles in a heat of steel would tend to inhibit grain growth and would be a factor in the resultant effects on the characteristics of the steel. There are, however, some effects obtained with the aluminum addition which do not seem to satisfactorily line up with the aluminum oxide dispersion theory, and it might be well to discuss some of them.

If it is aluminum oxide, why does time of addition play so important a part? In electric furnace steel which has already been very well deoxidized by ferromanganese and ferrosilicon additions, not to mention finishing under a reducing slag of very low FeO content, why is it so important that the aluminum addition be made within a very limited time before pouring?

In large open-hearth heats, why does the effect of the aluminum addition decrease rapidly near the end of the pour? If aluminum oxide, in colloidal submicroscopic suspension, is the primary cause of fine grain, grain growth control and hardenability control, why should the effect be so sensitive to time in the ladle? If this loss in effect is due to coalescence of the oxide particles, why, in the electric furnace, does fine grain scrap show a marked tendency to produce fine-grained heats *without* aluminum; or with very small aluminum additions, when dead melted? And why, in the electric furnace, does the simple act of "boiling down" a heat of fine grain scrap eliminate this fine-grain tendency?

If steels of relatively low oxide content exhibit the fine grain characteristics with relatively low aluminum addition, why is more aluminum required for the more highly oxidized steel? Thus Öhman[11] states that aluminum in much smaller amounts than is cus-

[11]Einar Öhman, *Jernkontorets Annaler*, Vol. 119, p. 143-74, 1935.

tomary in America, can definitely improve the hardening range of Swedish steels. He illustrates this by showing that less than 3 ounces of aluminum per gross ton added to a 1.10 per cent carbon electric furnace steel ingot definitely improves the grain growth characteristics and states that the depth of hardening is somewhat reduced by an addition of aluminum.

In American basic electric furnace practice where a so-called reducing slag is used under which to complete the deoxidation, it has been found that the amount of aluminum required to obtain a certain definite grain-size is less than in the basic open-hearth heats which are more highly oxidized. It might be argued that the same quantity and distribution of aluminum oxide should give the same grain-size and that no extra aluminum would necessarily be required, for the more highly oxidized heats unless a definite percentage of metallic aluminum in solution was required. If a critical amount or particle size of aluminum oxide is necessary as would be expected, how could increasing aluminum above the minimum, produce fine grain in over-oxidized heats? It seems rather doubtful if the delicate control implied by the necessity of obtaining critical particle size and distribution could be obtained at all in the highly oxidized heats, or that increasing aluminum to a uniformly higher amount would produce the same critical dispersion of oxide particles in the more highly oxidized basic open-hearth heats that would be obtained in the electric furnace heat with a lower aluminum addition.

It might be argued also that since the addition of approximately one pound of aluminum per ton will be sufficient to completely deoxidize or kill an ordinary open-hearth heat, no possible change could be made in the amount or size of the aluminum oxide with aluminum additions above one pound per ton. It is a well known fact, however, that in the ordinary well made basic open-hearth plain carbon heat which has been deoxidized with ferromanganese and ferrosilicon that considerably more than one pound of aluminum per ton in the ladle is required to obtain the very fine grain characteristics and that much higher additions than one pound per ton are required where the grain growth control specifications are exacting.

It seems more logical to assume that more highly oxidized heats require the excess aluminum to satisfy the oxide present and that the excess above that required to satisfy deoxidation requirements is necessary for grain growth control.

While it is difficult to prove, actual practice indicates that very

little effect in establishing fine grain characteristics is obtained by an aluminum addition until a certain definite minimum is added and then the fine grain effect is obtained very rapidly. This phenomenon can be checked by any melter who has tried to govern his practice to obtain intermediate grain-size control. He will insist that fine or coarse grain specifications are not so difficult to meet but that intermediate sizes are, in his opinion, "commercially impossible." This would indicate a very narrow range of particle sizes and dispersion, and if it is as difficult as the melter would insist, it would seem that it would be very difficut to obtain hundred-ton heats of steel with the remarkable uniformity of grain-size which can be now obtained in either the definitely coarse-grained or fine-grained types. One of the unexpected characteristics of grain-size control is this uniformity, and to those of us who have checked thoroughly the grain-size from the first molten steel in the furnace to the final products, there is nothing more remarkable than the fact that under normal conditions of processing that the variation in the McQuaid-Ehn grain-size is almost commercially negligible.

That this should be the case where we are depending upon the submicroscopic dispersion of infusible particles of a very definite critical size, is hard to believe. There is no doubt, of course, but what the presence of such particles would have an effect upon the grain-size, and hence play a part in the establishing of the grain-size and grain growth effects.

It would seem that the aluminum addition required to obtain certain grain growth characteristics in a heat of steel depends upon the degree of deoxidation of the bath before the addition is made, only to the extent that in order to obtain effects which are satisfactory, an excess of aluminum must be added over and above that required to satisfy deoxidation requirements. It is quite noticeable to anyone who is required to produce steel of fine grain type that the addition of manganese and particularly silicon tends to reduce the amount of aluminum required to obtain the fine grain characteristics.

Epstein[6] and others have discussed the fact that silicon increases the ease with which the fine grain type can be obtained by aluminum addition, showing clearly the effect of the presence of silicon and manganese in reducing the amount of aluminum required. Enlund in discussing a report by Öhman,[11] states that the aluminum addition alone is without effect—that only when the steel from the outset contains a minimum percentage of silicon or if the silicon is simul-

taneously added, that the steel exhibits resistance to grain growth. These observations in regard to silicon and its effect in combination with aluminum would indicate that a reduction in the amount of oxide present in the form of FeO in solution in the steel would make more effective the metallic aluminum in solution in the iron, due to the reduction in the amount of aluminum required to satisfy the oxide present. Certainly it would not seem that the explanation of the reduced aluminum required with the well deoxidized steel as compared to the more highly oxidized steel can be explained by the greater ease in obtaining submicroscopic particles of the critical size dispersed uniformly throughout a large heat of open-hearth steel.

At this point the theory that it is metallic aluminum and its effect on the austenite transformation and carbide solubility that is the primary factor in grain growth variation and normality fits better into the practice. It should of course be assumed that any addition or element which affects carbide (or carbon) solubility should have the same effect. Dealing with aluminum as we are, it is reasonable to explain the importance of the time factor by the activity of the oxidation reaction with aluminum at steel-making temperatures and argue that the loss of the aluminum effect in pouring open-hearth heats is due to the formation of aluminum oxide by oxidation under an open-hearth slag of fairly high oxide content. It can be argued that in dead melted electric furnace heats, the oxidation may be insufficient to reduce the metallic aluminum content below that necessary to affect the grain-size, so that the fine-grained dead melted charge may still remain fine-grained when melted. Also, on the other hand, the introduction of iron oxide in the form of ore to reduce the carbon would tend to reduce to a trace the metallic aluminum in the molten bath. It, of course, could be argued that the oxide particles would, in the case of the dead melted heat, be relatively unaffected whereas in the "boiled down" heat the physical action produced by the gas evolution or boil would result in coalescence of the oxide particles. Yet the fact that holding a fine grain basic open-hearth heat for a relatively short time (as compared to finishing an electric heat) in the ladle will cause a loss of the aluminum effect indicates that the cause is probably not physical.

That extremely small additions of oxide, etc., are active in affecting the carbide structure, is evident from the fact that in compound carburizing, according to Grossmann, oxygen is absorbed which is directly the cause of abnormality in heats containing low

manganese contents. He found that as the manganese increased, the oxygen absorbed decreased so that at manganese contents above one per cent little if any oxygen would be absorbed.

He also took samples which were abnormal when carburized in compound and by carburizing them in oxygen-free hydrocarbon gas demonstrated that they became normal. While no analysis was made of his samples for aluminum, it is quite certain that the aluminum content was very small, especially in the low manganese heats.

The gas used in the experimental work in developing the oxygen absorption theory was specially prepared and supposedly entirely free from oxygen. It is known to those who have had experience with both the commercial gas carburizing and the commercial compound carburizing that the abnormal type of steels was found when carburizing by either method on a commercial scale.

Table VIII
Effect of Carburizing Agent on Normality and Grain-Size

	Pot Carburized				Gas Carburized			
	1710 Degrees Fahr.		1800 Degrees Fahr.		1700 Degrees Fahr.		1800 Degrees Fahr.	
Heat	Case Grain-Size	Boundary Rating	Case Grain-Size	Boundary Rating	Case Grain-Size	Boundary Rating	Case Grain-Size	Boundary Rating
412	6–7	Abnormal	1–2	Sli. Abn.	6–7	Abnormal	6–7	Abnormal
321	6	Abnormal	6–5	Abnormal	6	Abnormal	6	Abnormal
212	7	Abnormal	6–7	Abnormal	6–7	Abnormal	6–7	Abnormal
312	7–6	Abnormal	7–6	Abnormal	6	Abnormal	6	Abnormal
411	7	Abnormal	7–6	Abnormal	7–6	Abnormal	7–6	Abnormal
313	7	Abnormal	7	Abnormal	7–6	Abnormal	7–6	Abnormal
223	7	Abnormal	8–7	Abnormal	8–9	Abnormal	8–9	Abnormal
324	7	Abnormal	7–6	Abnormal	7 few 5	Abnormal	7–8	Abnormal
423	6–4	Abnormal	5–2	Sli. Abn.	6–4 few 3	Abnormal	6–4 few 2	Abnormal
322	7	Abnormal	7–6	Abnormal	6–7	Abnormal	7	Abnormal
421	7	Abnormal	7–6	Abnormal	6–7	Abornmal	6–7	Abnormal
012	2–1	Normal	2–1	Normal	3–2	Normal	3–2	Normal
311	7	Abnormal	7–6	Abnormal	6	Abnormal	6	Abnormal
118	6	Abnormal	5	Normal	5–6	Abnormal	5 few 2	Abnormal
117	5	Normal	6	Sli. Abn.	6	Abnormal	6 few 5	Abnormal
114	7–6	Abnormal	6	Abnormal	7	Abnormal	6 few 2	Abnormal
115	7	Abnormal	7–6	Abnormal	7–8	Abnormal	7–8	Abnormal
413	6–2	Abnormal	6	Sli. Abn.	6–3	Abnormal	6–5 few 2	Abnormal
222	7–6	Abnormal	7–6	Abnormal	7–6	Abnormal	7–6	Abnormal
323	7–6	Abnormal	7–6	Abnormal	7	Abnormal	7–6	Abnormal
422	6	Abnormal	6–7	Abnormal	6–5	Abnormal	6–7	Abnormal

In an effort to check the effect of the carburizing agent on the normality and grain-size, twenty-one of the experimental heats were carburized in carburizing compound and samples from the same portion of the same bar from each heat were also carburized in a commercial gas carburizing furnace. The gas used in carburizing consisted principally of methane with ethane and other hydrocarbons up to 99 per cent. The balance was nitrogen with oxygen up to a maximum of 0.3 per cent. The sulphur was not more than a trace. The

compound-carburized pieces were carburized at 1700 degrees Fahr. (925 degrees Cent.) for 8 hours, cooled in the furnace to 800 degrees Fahr. (430 degrees Cent.) in 2.5 hours and then cooled in air. A second run was also made at 1800 degrees Fahr. (985 degrees Cent.) and cooled in a similar manner to determine the McQuaid-Ehn grain-size and structure at these two temperatures.

The gas-carburized runs* were made at 1700 degrees Fahr. (925 degrees Cent.) for 6 hours and at 1800 degrees Fahr. (985 degrees Cent.) for 5 hours at temperature. The work from the gas carburizing furnace was cooled slowly in mica. The gas for carburizing was on continuously from start to finish in an effort to prevent the presence of any oxygen from the atmosphere. Results of these runs are shown in Table VIII.

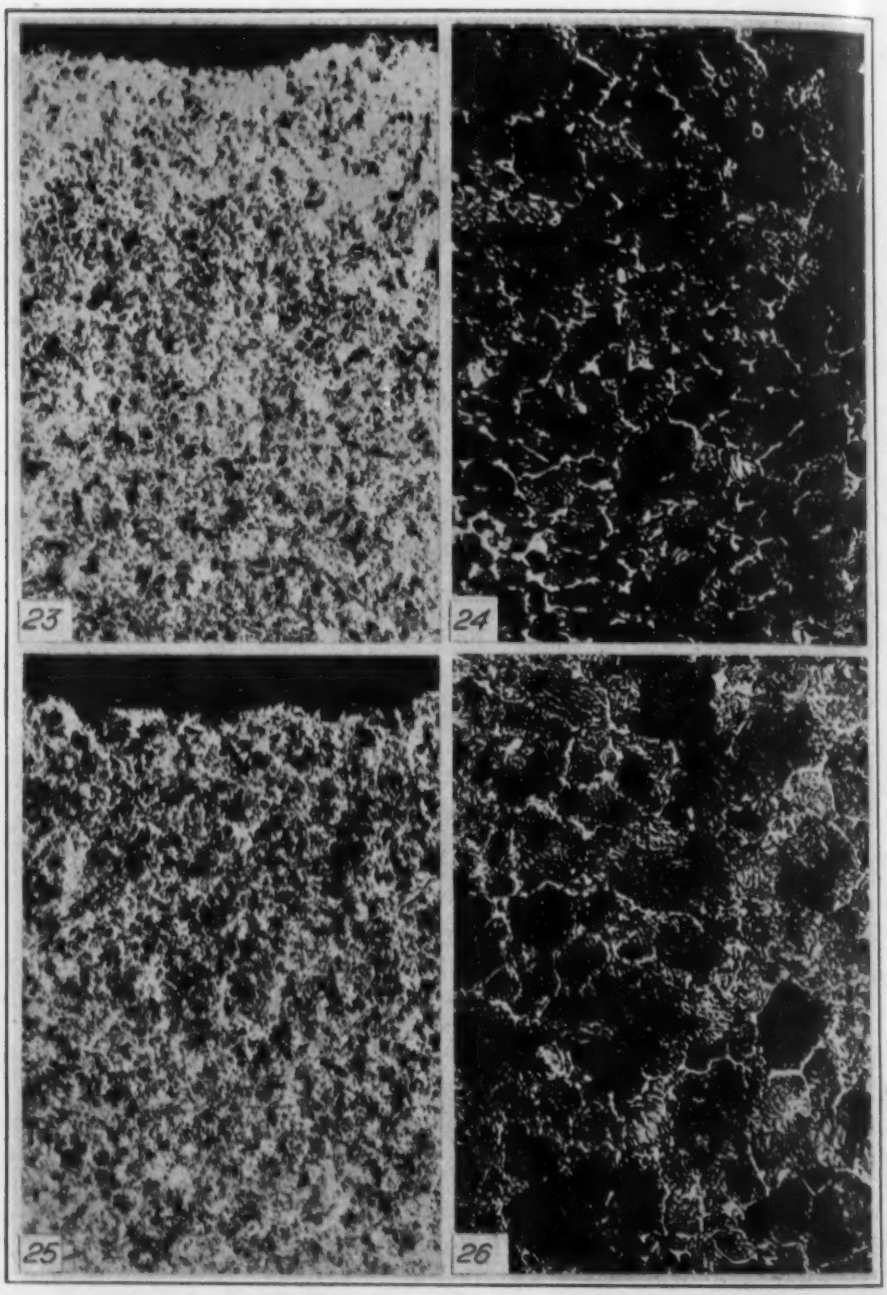
It will be seen from the Table that there is practically no difference in either the grain-size or normality from the gas carburizing or the compound carburizing. Figs. 23 to 26 show the standard McQuaid-Ehn tests at 100 diameters, heat 223 after gas carburizing at 1700 degrees Fahr. (925 degrees Cent.) and 1800 degrees Fahr. (985 degrees Cent.). Figs. 27 to 30 show the same samples after electrolytic etch in sodium picrate. It is very apparent that the gas carburizing as it was done had no effect on the structural abnormality or grain-size of the pieces carburized. It is of course not intended to imply that these same results would be obtained with the carburizing gases absolutely free from oxygen, but it is quite evident the absorbed oxygen effect must be due to the results of relatively minute quantities of oxygen. As a further check, samples from heat 324 and 423 were very carefully analyzed for oxygen before and after carburizing with the following results:

Table IX
Change in Oxygen Content in Pack-Carburizing

Heat	C	Mn	Si	Al	Oxygen Per Cent			
					Before	After	Decrease	
324	0.49	1.44	0.18	0.124	0.0865	0.0448	0.0417	Both Heats
423	0.49	1.41	0.25	0.046	0.0893	0.0635	0.0258	Abnormal

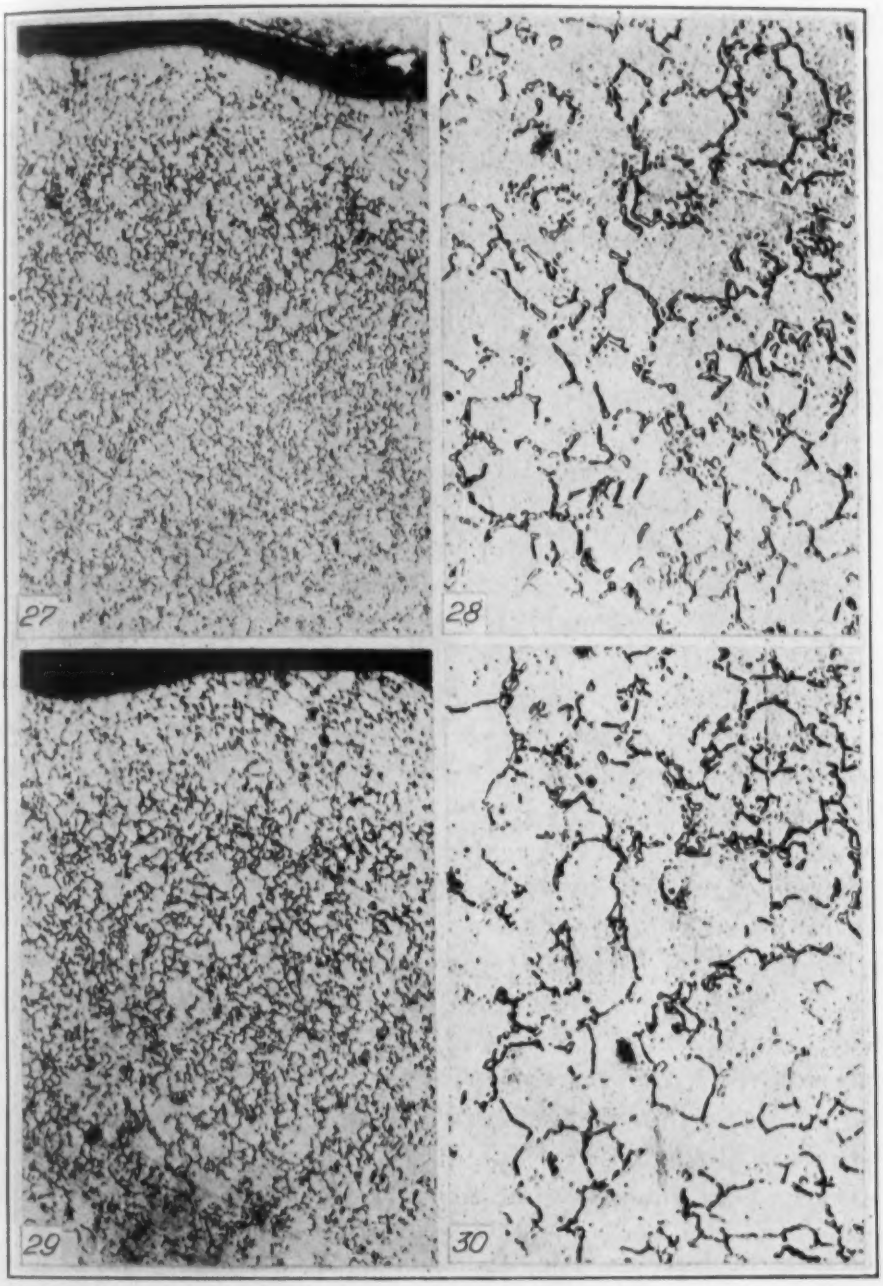
These oxygen values check with Grossmann's finding in that the heats in question were high in manganese and showed, not an absorption, but an evolution of oxygen. They do indicate that since oxygen was lost rather than absorbed during carburizing, that the

*Gas carburizing runs made by L. D. Gable, metallurgist, Timken Roller Bearing Co., Canton, Ohio.



Figs. 23 to 26—McQuaid-Ehn Carburizing Test (at 1710 Degrees Fahr.) Figs. 23 and 24 for Heat 223 at × 100 and × 500. Figs 25 and 26 are from the Same Heat Only Carburized at 1800 Degrees Fahr. × 100 and × 500 Respectively.

abnormal structure in these heats was not in any way connected with oxides formed during carburizing. Undoubtedly the abnormal structure found in these heats was due to aluminum. It is quite possible



Figs. 27 to 30—McQuaid-Ehn Carburizing Tests at 1710 Degrees Fahr. and 1800 Degrees Fahr. Electrolytic Etch in Sodium Picrate. Figs. 27 and 28 Carburized at 1710 Degrees Fahr. × 100 and × 500 Respectively. Figs. 29 and 30 Carburized at 1800 Degrees Fahr. × 100 and × 500 Respectively.

that the normal structure found in the heats carburized in hydrocarbon gas free from oxygen was due to the relatively slow carburizing action of such a gas where special means are not taken to remove

the soot formed in carburizing. If the carburizing action is slow enough, the solution in the austenite of the carbon or carbide formed may be fast enough to reduce the excess carbides to the point where they neither interfere with the grain growth or promote coalescence of the lamellar carbide at the grain boundary.

If we are to assume that it is the aluminum in the steel in addition to that required to satisfy the deoxidation requirements which is effective in obtaining the resistance to grain growth characteristics of so-called fine grain steel, how can we explain then the connection between this aluminum and the results obtained? Assuming that the characteristics of the steels to which aluminum has been added are evident by decreased grain-size and resistance to grain growth as well as decreased hardenability, we might assume that there is some connection between aluminum, hardenability and grain-size.

The most important factor in the hardening of steel as we know it today, is the carbon content, and we find as the carbon increases from zero to the eutectoid that it becomes easier to obtain higher and higher hardness by quenching. The fundamental requirement of hardening steel is to so control the speed of quenching that the rate of cooling within a limited range of temperature will be sufficiently high so as to completely suppress the pearlite transformation. These requirements have been most clearly and thoroughly covered by Bain[3] and others and are cited to center our interest for the moment on the fundamental requirement in hardening steel. It is apparently necessary in order to obtain satisfactory results from a rapid cooling, that we start from a solution of carbon (or carbide) in austenite and cool this at the critical rate mentioned above. Time is required to obtain solution of the carbon or carbide in the austenite and the time required varies not only with the carbide composition but also with the size and distribution of the carbide. Thus it is well known that spheroidized carbides are difficult to get into solution, and a higher temperature and more time is required when the carbon exists in this condition.

It is well known that the solubility of carbon or carbide in austenite varies with the composition of the austenite and the form in which the carbon is present. Vanadium carbides are particularly difficult to get into solution and vanadium steels quenched directly from the carburizing temperature will almost invariably show the presence on the surface of an extremely high concentration of almost pure carbides. This indicates that at the carburizing temperature and

under the conditions existing at the surface of the steel, these vanadium carbides were forming faster than the austenite absorbs the carbon from the carburizing agent, and with these steels it has been found advantageous to carburize at temperatures 50 to 100 degrees Fahr. (30 to 60 degrees Cent.) higher than would be considered proper for steels not containing vanadium.

One of the largest users of vanadium carburizing steel carburizes regularly at a temperature of 1775 degrees Fahr. (970 degrees Cent.) with very satisfactory results. The object of the higher carburizing temperature is to increase the solubility of the carbon in the austenite and to thereby prevent the building up of carbide at the surface in a form which is difficultly soluble at the carburizing temperatures. It also indicates that the austenite grain-size established as the steel passes through the critical range will tend to be fixed by the presence of difficultly soluble carbides which exist at the grain boundaries in the saturated outer zone. The presence of any substance (such as aluminum) in the austenite which would tend to decrease the solubility of the carbon or carbide in the austenite would tend to favor the formation at the lower carburizing temperatures of excess carbides around the austenite grain boundaries in the saturated zone.

Those carbide particles would tend to coalesce and become still more difficultly soluble and hence it is not at all impossible that under the usual conditions of carburizing that we have the building up of carbides in the boundaries of the saturated austenite grains at the lower carburizing temperatures which tend to restrict grain growth until a temperature is reached at which the solubility of carbon in the austenite has increased to the point where the carbide particles around the austenite grain boundaries will be absorbed.

We are all familiar with the tendency in quenched coarse-grained chromium steels of the carburizing grade to exhibit, when fractured, a fine martensitic hypereutectoid zone and a coarse martensitic gradation zone, indicating the inhibiting action of the difficultly soluble chromium carbides in the hypereutectoid zone.

An indication of the effect of carbides which resist solution is found not only in the case of vanadium steels, but also in most steels as far as is known, which are being carburized in an active carburizer. This indication is found in the fact that as a rule the hypereutectoid zone in a carburized piece resists grain growth to a higher temperature than the gradation zone or core. While many grain growth carburizing tests have been made, the speaker has yet to see

one plain carbon heat or vanadium steel heat where the core coarsened at a higher temperature than the case. Almost invariably the core would coarsen at a temperature from 100 to 150 degrees Fahr. lower than the hypereutectoid zone. Grossmann[12] mentions cases where the hypereutectoid zone coarsens at a lower temperature than the core, but offers no explanation of the phenomenon. Certainly it is difficult to explain by the presence of submicroscopic particles of aluminum oxide. It is also difficult to explain by attributing grain growth inhibition to aluminum and its effect on austenite solubility of carbides.

It is believed that those cases in which the grain-size of the case coarsens before the grain-size in the core, occur in steels in which the grain begins to coarsen at temperatures close to the Ac_3 point. These are steels in which the carbides are of such size and distribution that they are more easily dissolved in the austenite as compared to steels in which we have aluminum or other additions in solution to increase the tendency of the carbides to coalesce.

It would be expected in steels of this type in which the grain coarsens close to the Ac_3 point, that the higher carbon case would coarsen ahead of the lower carbon core because of the greater differential between the coarsening temperature and the Ac_3 point.

The temperature and rate at which the carbide particles will be absorbed depends principally upon their sizes, composition and the presence in the austenite of some element which tends to affect their solubility. Upon cooling, if the austenite transformation takes place at a high enough temperature so that carbides are precipitated while the ferrite is sufficiently mobile to permit coalescence at a time when the transformation is slow enough, either lamellar pearlite or spheroidized carbide and ferrite or an intermediate stage of partly diffused (coalesced) carbide may be the result. Lamellar pearlite results when the carbide is precipitated at such a rate or in a mobile enough ferrite that coalescence starts in the form of plates from many points in the *pearlite* grain. If the transformation is at such a temperature and rate that the carbide not only has time to form plates but to coalesce further, the carbides will, in a hypereutectoid steel, coalesce on the boundary carbides those plates in contact with the boundary carbides, leaving the center of the pearlite grain lamellar and forming the familiar abnormal rim.

In other words, the so-called abnormal type of structure is prob-

[12] M. A. Grossmann, "On Grain-Size and Grain Growth," TRANSACTIONS, American Society for Steel Treating, Vol. 21, December, 1933, p. 1079.

ably due to coalescence of the carbide plates in contact with the boundary carbide under conditions of time and temperature of the ferrite which will permit it. The tendency of the carbide plates in contact with the boundary carbides to coalesce and leave a ferrite rim would vary with different heats, depending upon the speed and temperature of the transformation of the austenite, which in turn would be affected by several factors such as aluminum, iron oxide, iron sulphide, etc., in solution in the austenite.

The presence of manganese, nickel, etc., which would tend to stabilize the austenite would reduce the tendency to coalesce the carbide, due to the greater rigidity of the ferrite at the lower temperature of transformation. Thus the higher manganese steels would tend to be more normal than the lower manganese steels. For the same reason it is evident that any carburized steel having a hypereutectoid zone would, upon sufficiently slow cooling, develop an abnormal structure as shown by Dr. Grossmann in his Campbell Memorial Lecture. It is believed that this building up of the carbide plates which touch the boundary carbide, will be greater or less, depending upon the rate of rejection of the carbide from the ferrite and the rigidity of the ferrite. If the rate of rejection is slow enough and the ferrite temperature high enough, coalescence will start at many points in the pearlitic grain, the lamellae thickening to the point finally where we have complete spheroidization. It is easy to see that we may have various degrees of carbide coalescence in a slowly cooled steel and that this coalescence depends primarily on the mobility of the ferrite and the rate of rejection of the carbide.

In a lower carbon steel, the coalescence of the carbide on the boundary would naturally be absent, and as before would occur finally within the pearlitic grain to form spheroidized carbide. It is probable that aluminum in solution in the austenite increases the speed of carbide rejection and decreases the carbide solubility in the ferrite. At the same time it would increase the speed and temperature of the austenite transformation, a phenomenon which has been observed to be characteristic of the abnormal steel, and accounts for the more shallow hardening of this type of steel.

The greater tendency for the carbides to coalesce in steels to which aluminum has been added as evidenced by the abnormal structure, does not indicate at first glance the logical explanation of the relation of grain-size to the coalescence of the carbide. On heating, however, it is believed that the aluminum in solution in the austenite

will decrease the carbide solubility, and due to the tendency of the carbides to exist in these steels in the more coalesced form, the carbides will be more difficult to dissolve. It is quite possible that there is a considerable tendency for the carbides in the steels containing aluminum to coalesce rapidly in the ferrite at temperatures just before the transformation to austenite. This would be the reverse phenomenon from that met with in cooling and would develop carbides not only difficult to get into solution, but which would act as inhibitors to grain growth until a temperature had been reached in which they became readily soluble in the austenite.

Herty[13] has shown that the rate of heating through the transformation range has a pronounced effect on the recrystallization rate of silicon-killed plain carbon steels. Very little grain refinement occurs when heating rates faster than 9 degrees Fahr. (5 degrees Cent.) per minute are used, but below this rate grain refinement *increases* as the rate of heating *decreases*.

Aluminum-killed steels show strongly marked grain refinement regardless of heating rate. This important phenomenon can be explained by the increasing coalescence of the carbide in the ferrite, of the silicon-killed steel, which occurs with increase in time at the temperature of the transformation. With the aluminum-killed steel, the coalescence occurs even at the fastest rate of heating which is possible.

It should be remembered at this point that the austenite transformation rate, both on heating and cooling, is affected by the presence of carbides, nonmetallic inclusions, mechanical stresses, etc., so that the grain growth inhibiting action of the carbides out of solution is also affected by these factors. Thus we may have in steels which are mechanically worked within the critical range, or just above the critical range, stresses in individual grains or groups of grains which facilitate the solution of carbides and thereby tend to form coarse grains in an otherwise fine grain structure. This produces the so-called duplex structure which is directly connected with mechanical workings. The presence of oxides and probably nitrides, etc., would have the effect of decreasing the carbide solubility and hence also acting as grain growth inhibitor.

The tendency of the aluminum addition to cause heavier car-

---

[13]C. H. Herty, Jr., D. L. McBride, S. O. Hough, "The Effect of Deoxidation on Grain-Size and Grain Growth in Plain Carbon Steels," Mining and Metallurgy Cooperative Bulletin No. 65, Pittsburgh, 1934.

bide particles in the ferrite would require, of course, a more rapid cooling in order to obtain the finer carbide distribution necessary to produce martensitic or fine pearlitic structure. The tendency to coalesce the carbides and to form thereby a pearlitic structure would be overcome by such additions as manganese and nickel which would lower the austenite transformation rate to the point where the rigidity of the ferrite interferes with the carbide coalescence. Thus it would be possible, by the addition of manganese, to obtain with ordinary quenching the necessary hardness in a steel containing aluminum. On heating this steel, moreover, coalescence would take place at the temperature of transformation and the heavier carbide particles would, as before, tend to inhibit grain growth so that with the high manganese steels we get the benefit of the deeper hardening properties and at the same time the fine grain structures which are characteristic of the steels containing aluminum.

The addition of any of the deeper hardening elements to steel containing aluminum would produce a result similar to that of manganese, so that the benefits of the aluminum addition to the alloy steels would still be worth while.

It is interesting to consider here the opinion of Professor Edward De Mille Campbell on the subject which we have just discussed. In a letter to Ehn in 1921 in which he discussed the subject of carbide stability in the so-called "abnormal" type of steel, Professor Campbell expresses himself as follows:

"In normal steel above the critical point the carbides form a homogeneous, probably colloidal solution, which persists until the critical point is reached, when, as the gamma iron goes over to the alpha state, in which the carbides are but slightly soluble, the precipitated carbides assume the form of thin plates, characteristic of normal pearlite. It is well known that the addition of a comparatively small amount of an electrolyte to any colloidal solution in water will bring about coagulation or flocculation of the colloid, and I think it not improbable that the dissolved oxides in your abnormal steels function in a manner exactly analogous to that of electrolytes in aqueous solutions, thus bringing about the flocculation or coalescence of the carbides, either before transformation takes place or during the critical period."

It is not intended to claim at this time that the grain growth characteristics, the hardenability characteristics or the abnormality characteristics are due to either the presence of submicroscopic

alumina particles or to the effect of aluminum on the austenite transformation rate and rate of carbide coalescence. The explanation that aluminum influences the hardenability and grain growth characteristics by its effect on the coalescence of the carbides precipitated when the austenite transforms, is simply offered as an hypothesis which seems to have a somewhat closer agreement to practice than would seem to be the case if we tried to explain these phenomena on the basis of submicroscopic alumina dispersion.

It is offered simply as a suggestion and only as an hypothesis in the hope that it might lead to a more general discussion and investigation of the behavior of aluminum when added in relatively small quantities to the commercial heats of steel.

In conclusion, it might be well to stress, a little, the fact that steel-making is after all still an art, and that we must turn over to a few well-trained men the problem of reducing a mixture of more than one hundred tons of miscellaneous (but selected) scrap, pig iron, limestone, etc., to a condition where it represents a valuable and usable high quality product, checked and inspected on every hand and which must not only meet close chemical specifications, but must harden deep enough but not too deep; must not warp too much, or crack in quenching, must machine well, must pass microscopic and macroscopic cleanliness tests, must pass so-called impact tests, transverse tests, grain-size tests, etc.

This modern miracle must be accomplished under the most difficult of working conditions at temperatures close to 3000 degrees Fahr. (1650 degrees Cent.), at which the very furnace itself is being destroyed in the making of the steel, a temperature at which the refractories used in ladle and runner are short lived, and at which reactions proceed at incredible speeds, particularly those involving oxidation. Yet under these adverse conditions, and with all the care involved in the selection of the personnel, equipment and materials, the success or failure of the result depends on being able to control the physical condition in the steel as it solidifies, of the addition to the steel of up to one part in one thousand of the most active of all the metallic elements that we know of, i.e., aluminum.

Truly we cannot give too much credit to the man on the open-hearth floor.

HARDENING CHARACTERISTICS OF ONE PER CENT CARBON TOOL STEELS*

By T. G. Digges and Louis Jordan

Abstract

Two commercial 1 per cent carbon tool steels were selected from widely used brands of one foreign and five domestic manufacturers. Selection of the two steels was made for their widely different depth of hardening characteristics. Specimens of each steel were prepared with three different initial structures, viz., spheroidized cementite, coarse pearlite, and sorbite, and a study made of the effect of these initial structures on the austenitic grain-size and grain-growth characteristics and on the critical cooling rates. These data also made possible a direct comparison of the relations between austenitic grain-size and critical cooling rate of the two steels over a range of quenching temperatures of 1425 to 1775 degrees Fahr. (775 to 970 degrees Cent.).

Introduction

THE past five years have witnessed the removal of much of the mystery that for many preceding years had surrounded the causes of marked differences in the hardening characteristics of steels of apparently identical chemical compositions. Davenport and Bain[1] pictured the structure and hardness developed in a quenched steel as dependent primarily on the particular temperature at which austenite decomposed during the quenching. The rate at which the steel was cooled during the quench was important only in determining to how low a temperature austenite could be cooled before its decomposition began. The hardenability of a steel is then pictured as determined by the stability of quenched austenite in the temperature range 1110 to 930 degrees Fahr. (600 to 500 degrees Cent.), the upper range in which austenite is most prone to decompose and

*Publication approved by the director of the National Bureau of Standards of the U. S. Department of Commerce.

[1]E. S. Davenport and E. C. Bain, "Transformation of Austenite at Constant Sub-Critical Temperatures," *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930, pp. 117-154.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The authors, T. G. Digges and Louis Jordan, are members of the metallurgical staff of the National Bureau of Standards, Washington, D. C. Manuscript received June 5, 1935.

in which its decomposition products are relatively soft. If the austenite of a particular steel is relatively stable in this temperature range and can be cooled through this range by a mild quench, then it decomposes only in the range below about 300 degrees Fahr. (150 degrees Cent.), the product of decomposition is martensite, and the steel is fully hardened. Such a steel may, therefore, be called a "deep-hardening" steel as compared with another the austenite of which is less stable in the range, 1110 to 930 degrees Fahr. (600 to 500 degrees Cent.), and which, therefore, does not fully harden under identical quenching conditions.

Bain[2] further clarified the conception of hardenability by suggesting that the factors which determine the relative stability of austenite in the temperature range 1110 to 930 degrees Fahr. (600 to 500 degrees Cent.) are (1) its chemical composition, and (2) its grain-size.

The control of austenitic grain-size and the far-reaching effect of such grain-size have been discussed in a number of recent papers, notably those of the "Grain-Size Symposium" of the American Society for Metals.[3] Steels of controlled grain-size have become commercially available.

The Hardening of Carbon Tool Steels

The so-called "body" or "personality" of tool steel as evidenced by depth of hardening and fracture tests has long been recognized as an important factor in the hardening of carbon tool steels. In papers presented before this Society in 1929, both Shepherd and Luerssen discussed variations in the hardenability of tool steel. Shepherd[4] described a simple test for depth of hardness penetration and Luerssen[5] pointed out the desirability, as well as the possibility, of controlling melting conditions to produce carbon tool steel with a predetermined hardness penetration and quenching temperature range. Such tool steels were shortly made available commercially.

The conception of the hardenability of tool steel as dependent upon austenitic grain-size rapidly became widely accepted. The in-

---

[2]E. C. Bain, "Factors Affecting the Inherent Hardenability of Steel," Transactions, American Society for Steel Treating, Vol. 20, Nov. 1932, p. 385-428.

[3]Transactions, American Society for Metals, Vol. 22, Dec. 1934.

[4]B. F. Shepherd, "Inherent Hardenability Characteristics of Tool Steel," Transactions, American Society for Steel Treating, Vol. 17, Jan. 1930, p. 90-110.

[5]G. V. Luerssen, "Some Notes on the Behavior of Carbon Tool Steel on Quenching," Transactions, American Society for Steel Treating, Vol. 17, Feb. 1930, p. 161-198.

fluence of the "initial structure" of the steel (the structure prior to heating for hardening) upon the austenitic grain-size, and hence upon the hardenability, was also recognized by those most active in developing the theories of grain-size effects. This factor has, however, received less attention than many other phases of austenitic grain-size influence.

Shepherd[6] has recently called particular attention to the dependence of "penetration-fracture characteristics" of tool steel on the heat treatment and the microstructure of the steel prior to the heating for hardening.

The experimental work to be described in this paper was done as a part of a comprehensive study of the characteristics of commercial 1 per cent carbon tool steels. Particular attention was given to the influence of the initial or prehardening structure upon the grain-size and grain-growth characteristics of austenite in and above the usual ranges of hardening temperatures for the steels considered.

Materials

Plain carbon tool steels, of about 1 per cent carbon, all representing widely used brands, were purchased through regular channels of supply from one foreign and five domestic manufacturers. Depth of hardening tests were made on initially spheroidized specimens by quenching three-quarter inch rounds in brine from two temperatures, 1425 and 1550 degrees Fahr. (775 and 845 degrees Cent.), and etching a section to show the hardness penetration. On the basis of these tests the two steels were selected which, while having very similar depth of hardening on quenching from 1425 degrees Fahr. (775 degrees Cent.) (within the usual hardening range) showed in one steel the least change, and in the other steel the greatest change in depth of hardening on increasing the quenching temperature to 1550 degrees Fahr. (845 degrees Cent.). The hardened and etched sections of these two selected steels are shown in Fig. 1. Steel 65 obviously has markedly changed in its hardenability as a result of increasing the quenching temperature from 1425 to 1550 degrees Fahr. (775 to 845 degrees Cent.) while steel 68 has changed very little. Steel 68 was, in fact, a steel produced under conditions which resulted in control of austenitic grain-size and was marketed with specific claims as to its uniformity in depth of hard-

[6]B. F. Shepherd, "The P-F Characteristic of Steel," Transactions, American Society for Metals, Vol. 22, Dec. 1934, p. 979-1016.

ening by quenching within and above the usual quenching temperature ranges. In this paper these two steels are occasionally indicated by the terms "shallow hardening" or "controlled grain-size" applying to steel 68 and "deep hardening" or "non-controlled grain-size" as applied to steel 65. The chemical compositions of the two steels, as

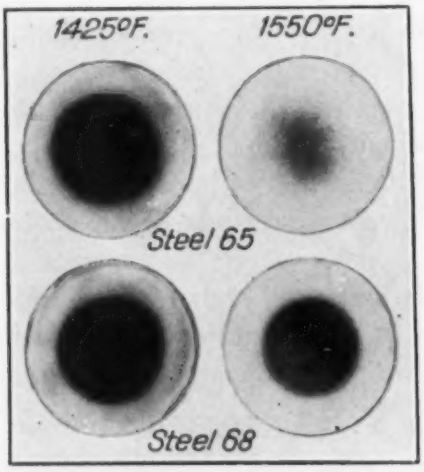


Fig. 1—Relative Depth of Hardening of Steels 65 and 68 Quenched from 1425 and 1550 Degrees Fahr. (775 and 845 Degrees Cent.). ¾-inch Rounds Quenched in Brine. Etched in 1 Per Cent Nitric Acid in Alcohol to Darken the Unhardened Portions.

shown in Table I, differed chiefly with respect to their content of aluminum or aluminum oxide. The controlled grain-size steel 68 contained appreciably greater proportions of both metallic aluminum (that portion soluble in acid) and Al_2O_3 than steel 65.

Table I
Chemical Composition of Steels with Different Hardening Characteristics.

Steel Ident. No.	Chemical Composition—Per Cent by Weight							
	C	Mn	P	S	Si	Cr	Ni	W
65	1.05	0.28	0.019	0.013	0.22	0.08	0.13	N.D.*
68	1.06	0.26	0.013	0.011	0.19	0.09	0.10	N.D.

Steel Ident. No.	Chemical Composition—Per Cent by Weight							
	Mo	V	Al_2O_3	Acid Soluble Al	Total Al	H	O	N
65	<0.01	<0.01	0.006	0.001	0.004	0.0002	0.007	0.009
68	<0.01	<0.01	0.010	0.008	0.013	0.0003	0.009	0.007

*N.D. = not detected.

Comparison of Deep Hardening and Shallow Hardening One Per Cent Carbon Tool Steels

The present paper will be limited to consideration of the effects of the initial (prehardening) structure of the two selected steels on their austenitic grain characteristics and on their critical cooling rates. Comparisons of these steels were also made with respect to their behavior in the transformation temperature ranges during thermal analyses, their relative rates of spheroidization, their impact strengths, their relative susceptibility to grinding cracks, their performance as tools in lathe cutting and the effect of rate of heating to the hardening temperatures. Details of these tests will be given in a later report.

Each of the two steels was treated to give three initial structures differing in the size and distribution of cementite. These three types of initial structure are illustrated, for each of the two steels, in Fig. 2. The spheroidized structure was obtained by annealing at 1425 degrees Fahr. (775 degrees Cent.); the coarse lamellar pearlite by heating spheroidized ¾-inch bars at 1750 degrees Fahr. (955 degrees Cent.) for 1 hour and cooling in the furnace; and the fine pearlite or sorbitic structure by heating spheroidized ¾-inch bars to 1750 degrees Fahr. (955 degrees Cent.) for 1 hour and cooling in air.

Austenitic Grain-Size Characteristics

The austenitic grain-size and grain-growth characteristics were determined for each steel starting with each of the three initial structural conditions. The specimens used for both grain-size and critical cooling rate determinations were ¼-inch square by 0.040 inch thick. One wire of a 22-gage chromel-alumel thermocouple was spot welded to the center of each of the two flat faces of each specimen. The specimens were heated in an atmosphere of dry nitrogen to the temperatures at which it was desired to determine the austenitic grain-size, held at that temperature for 15 minutes and then cooled in a manner suitable for outlining the grains. If the temperature establishing the grain-size was above the A_{cm} temperature, a cementite network outlining the austenite grains was produced by slowly cooling the specimen to about 1400 to 1375 degrees Fahr. (760 to 745 degrees Cent.) and holding it a short time at that temperature before quenching. If the temperature establishing the grain-size was between the $A_{3,\,2,\,1}$ and A_{cm} temperatures then the specimen

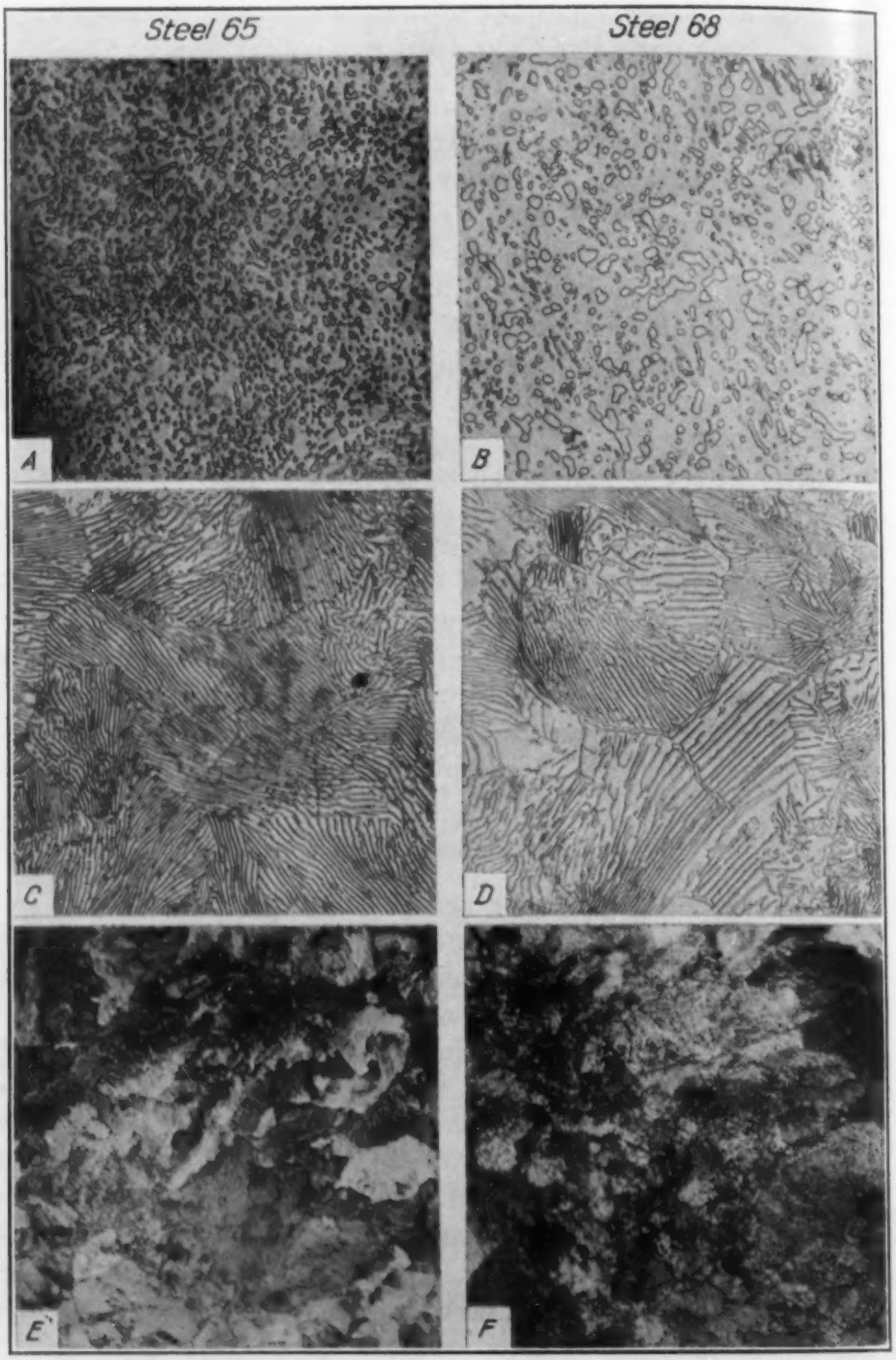


Fig. 2—Initial Structure of Steels 65 and 68. A and B, Spheroidized Cementite. C and D, Coarse Lamellar Pearlite. E and F, Fine Pearlite or Sorbite. Etched in 1 Per Cent Nitric Acid in Alcohol. × 500.

was quenched under conditions which permitted the formation of just sufficient primary troostite to outline the austenitic grain. The grain counts were made by Jeffries' method.[7]

The relations between austenitic grain-size and temperature for the two steels in the three different initial structural conditions are shown in Fig. 3. At the highest temperatures at which measurements were made, namely, 1750 to 1775 degrees Fahr. (955 to 970 degrees Cent.), each steel developed a rather characteristic grain-size which was independent of the initial structural condition. In this

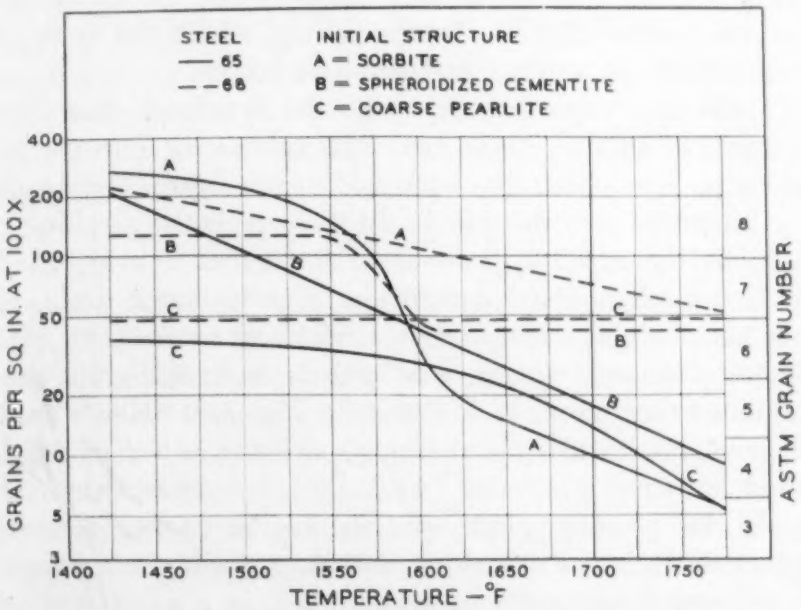


Fig. 3—Relation of Austenitic Grain-Size to Temperature for Steels 65 and 68 with Different Initial Structures.

temperature range, the controlled grain-size steel had an A.S.T.M. grain-size number of 6 to 7 and the non-controlled grain-size steel of 3 to 4. The grain-size–temperature curves separate into two characteristic groups only at temperatures above 1600 degrees Fahr. (870 degrees Cent.), that is, above the temperature of the A_{cm} line and in the range in which all cementite is presumably in solution in the austenite. At temperatures from 1425 to 1600 degrees Fahr. (775 to 870 degrees Cent.), the range in which the structure consists of austenite and cementite, the grain-size is noticeably dependent on the initial structure as well as on the temperature. The non-controlled grain-size steel 65, which is characteristically coarse-grained

[7]American Society for Testing Materials Standards, 1933, Pt. 1, p. 902, Note 2.

at 1750 degrees Fahr. (955 degrees Cent.), had a very fine grain at 1425 degrees Fahr. (775 degrees Cent.), if its initial structure prior to heating was either spheroidized or sorbitic. Each steel, with initially spheroidized or sorbitic structure, had a smaller grain-size at 1425 degrees Fahr. (775 degrees Cent.) than did the steels with an initial coarse, pearlitic structure. The two steels, with similar initial structures, had austenitic grain-sizes of the same order of magnitude at 1425 degrees Fahr. (775 degrees Cent.). In the two cases in which sharp inflections occurred in the grain-size–temperature curves, they were in the temperature range of 1550 to 1600 degrees Fahr. (845 to 870 degrees Cent.), where the completion of the solution of the separate carbide phase occurs.

These results are consistent with the hypothesis that the greater the degree of subdivision of cementite on heating into the temperature range just above the eutectoid temperature, the smaller the austenitic grain-size established. In both steels the sorbitic structure established the smallest grain at 1425 degrees Fahr. (775 degrees Cent.), the spheroidized structure a slightly larger grain, and the coarse lamellar pearlitic structure a relatively coarse grain. Because each steel ultimately reached a definite characteristic grain-size at the maximum temperature, as is shown in Fig. 3, it follows that, for a given steel, the initial (prehardening) structure which establishes the smallest austenitic grain-size (e.g., at 1425 degrees Fahr.) also undergoes the greatest grain growth at the higher temperatures. Whether this subsequent growth took place steadily and progressively with increasing temperatures or occurred as a more rapid growth over a restricted range of temperature did not appear to be determined by the initial structure. Thus, in the non-controlled grain-size steel 65 rapid growth over a restricted temperature range occurred only in the specimens initially of a sorbitic structure. A similar rapid growth over a small range of temperature occurred only in the spheroidized samples of the controlled grain-size steel 68.

Critical Cooling Rates

The critical cooling rates were determined for specimens representing the entire range of austenitic grain-sizes developed in each steel from each of the three initial structures. The critical cooling rate was taken as the average cooling rate between 1110 and 930 degrees Fahr. (600 and 500 degrees Cent.) when the structure of

the quenched specimen was martensite containing nodular troostite in proportions estimated to be between 1 and 3 per cent. The specimens for the critical cooling rate determinations were of the same shape and size as those used for grain-size determinations and were heated in the same manner, held for the same time at the temperature establishing the austenitic grain-size and were then quenched directly from that temperature into a suitable quenching medium contained in a bath which sealed the bottom end of the vertical tube of the heating furnace. A photographic time-temperature curve was obtained during the quench in the manner previously described by French and Klopsch.[8] Examination of the microstructure of the quenched specimens was made on a cross section of the 0.040 inch thick sheet near the point of contact of the thermocouple wires.

Fig. 4 shows the relations between the critical cooling rate and the quenching temperature (which was also the temperature establishing the austenitic grain-size) for these two steels. When quenched from 1425 degrees Fahr. (775 degrees Cent.), the critical cooling rates for the two steels were approximately the same whether the initial structures were sorbitic or spheroidized, that is, the steels hardened with equal facility. The critical cooling rates for the two steels were also the same when the initial structure was coarse pearlite, but this rate was much lower than that of the initially sorbitic or spheroidized steels.

With quenching temperatures in the lower range—1425 to about 1600 degrees Fahr. (775 to 870 degrees Cent.)—the critical cooling rate for either steel is clearly influenced by the initial structure. Above 1600 degrees Fahr. (870 degrees Cent.) the curves separate into two groups (one for each steel). At 1725 to 1750 degrees Fahr. (940 to 955 degrees Cent.), critical cooling rates are obtained which appear to be characteristic of the steels, irrespective of their initial structure. At this temperature a definitely faster critical cooling rate is obtained for the controlled grain-size steel 68, regardless of its initial structure, than for the non-controlled grain-size steel 65. The general course of the curves of Fig. 4 parallels the grain-size characteristics of the two steels as represented in Fig. 3, the faster critical cooling rate corresponding with the finer grain-size for steel 68 at about 1750 degrees Fahr. (955 degrees Cent.), and the initial structure exercising its effects chiefly in the temperature range below

[8] H. J. French and O. Z. Klopsch, "Quenching Diagrams for Carbon Steels, etc.," TRANSACTIONS, American Society for Steel Treating, Vol. 6, 1924, p. 251-94.

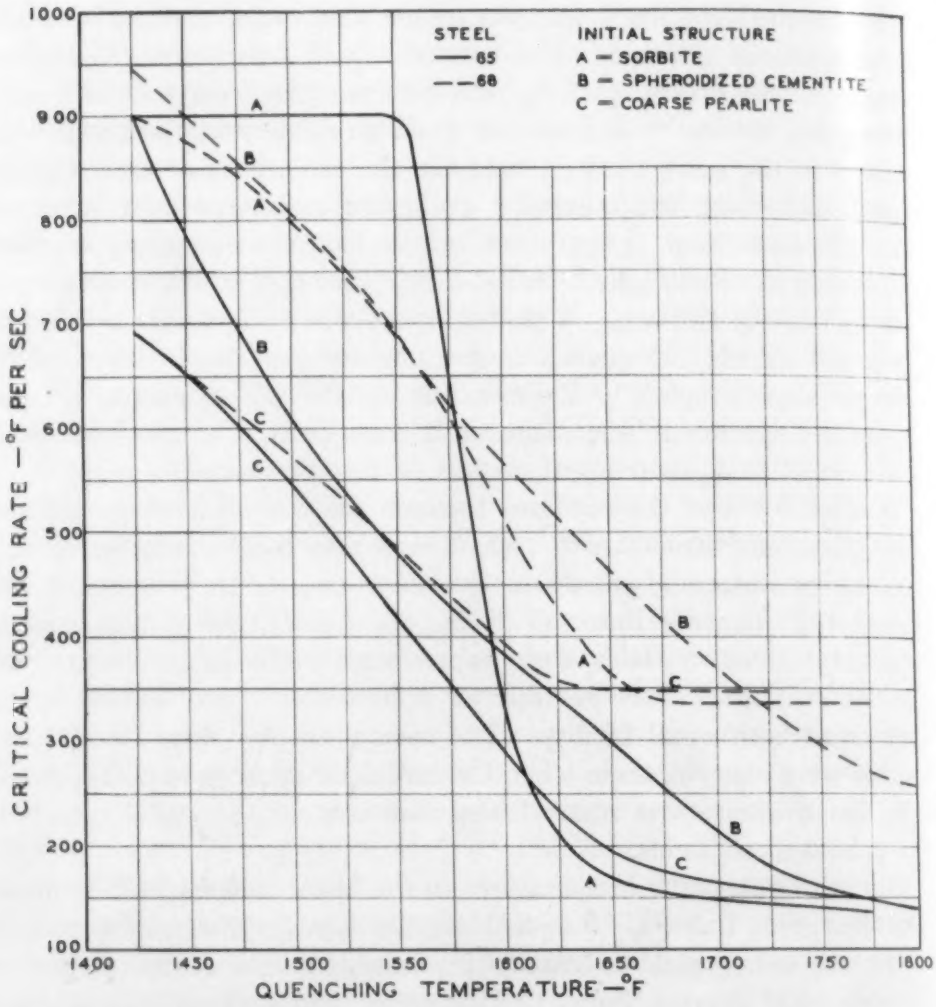


Fig. 4—Relation of Critical Cooling Rate to Quenching Temperature for Steels 65 and 68 with Different Initial Structures.

1600 degrees Fahr. (870 degrees Cent.), where the cementite is not entirely dissolved.

The significance of the curves of Fig. 4 in the lower range of temperatures is interesting and is illustrated by Fig. 5. Both the specimens shown in Fig. 5 are ¾-inch rounds of steel 65 which have been quenched in brine. Specimen A was quenched from 1500 degrees Fahr. (815 degrees Cent.) and Specimen C from 1425 degrees Fahr. (775 degrees Cent.). A higher quenching temperature normally results in deeper hardening, especially in a non-controlled grain-size steel such as steel 65. It is obvious, however, that Specimen A has hardened less deeply than Specimen C. This difference is

due to the different initial structures of the specimens, A having initially a sorbitic structure and C a coarse pearlitic structure. Fig. 4 shows that a critical cooling rate of 900 degrees Fahr. (480 degrees Cent.) per second is obtained for Specimen A quenched from 1500 degrees Fahr. (815 degrees Cent.) while a critical rate of approximately 700 degrees Fahr. (370 degrees Cent.) per second is obtained for Specimen C quenched from 1425 degrees Fahr. (775 degrees

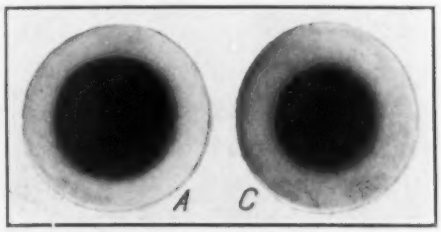


Fig. 5—Relation of Critical Cooling Rate to Depth of Hardening. A, Steel 65, ¾-inch Round, Initially Sorbitic, Quenched in Brine from 1500 Degrees Fahr. (815 Degrees Cent.). C, Steel 65, ¾-inch Round, Initially Coarse Pearlite, Quenched in Brine from 1425 Degrees Fahr. (775 Degrees Cent.).

Cent.). Obviously, depths of hardening of specimens of similar size and shape are indicated by critical cooling rates, the lower rates being equivalent to the deeper hardening, and the curves of Fig. 4 may be used as an index of the relative depths of hardening.

The curves of Fig. 4 for the spheroidized initial structure of the two steels simply reflect the basis upon which the two steels were selected, namely, that with this initial structure, the steels have the same depth of hardening at 1425 degrees Fahr. (775 degrees Cent.), but very different depths of hardening at 1550 degrees Fahr. (845 degrees Cent.), steel 65 being the deeper hardening steel. With this in mind the significance of initial structure is well illustrated by the fact that steel 68 with an initial coarse pearlitic structure is a much deeper hardening steel at 1425 degrees Fahr. (775 degrees Cent.) than steel 65 either spheroidized or sorbitized, and remains far more deeply hardening than steel 65 of initially sorbitic structure at all temperatures up to 1600 degrees Fahr. (870 degrees Cent.). Again, steel 65 initially sorbitized is a more shallow hardening steel than any of the other specimens at all quenching temperatures up to 1550 degrees Fahr. (845 degrees Cent.), while above 1600 degrees Fahr. (870 degrees Cent.) steel 65, in any initial structure, is the deeper hardening steel. Only with quenching temperatures of 1650 degrees

Fahr. (900 degrees Cent.) and above is steel 68 consistently a more shallow hardening material than steel 65.

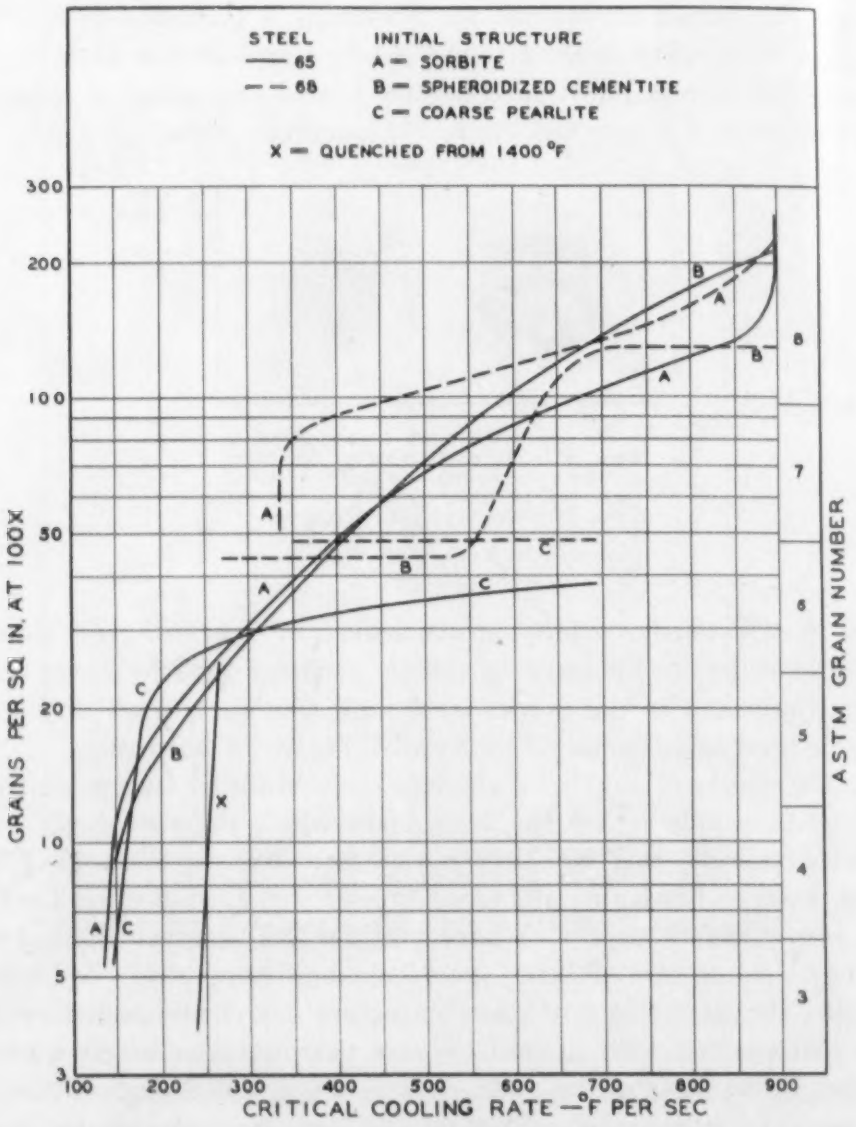


Fig. 6—Relation of Austenitic Grain-Size to Critical Cooling Rate for Steels 65 and 68 with Different Initial Structures.

Relation of Critical Cooling Rate to Austenitic Grain-Size

The general similarity and correlation of the grain-size–temperature curves of Fig. 3 and the critical cooling rate-temperature curves of Fig. 4 have already been pointed out. The data of these two

figures permit a direct comparison of austenitic grain-size and critical cooling rate as shown in Fig. 6.

The data as presented in Fig. 6 show that the critical cooling rate for steel 65, the non-controlled steel, with either spheroidized or sorbitic initial structure, in general, increases with decreasing austenitic grain-size (increasing grain-size number). The relationship between the austenitic grain-size and the critical cooling rate for steel 65 was influenced by the initial structure only in the lower range of quenching temperature (the smaller grain-size), where all the carbon was not dissolved in the austenite. For example, a critical cooling rate of approximately 700 degrees Fahr. (370 degrees Cent.) per second was obtained for the non-controlled grain-size steel 65 under the following conditions:

	Initial Structure	Quenching Temperature Degrees Fahr.	Austenite Grains Per Sq. In. at × 100	A.S.T.M. Grain Number
(A)	Fine lamellar pearlite or sorbite...	1570	100	8
(B)	Spheroidized cementite	1475	130	8
(C)	Coarse lamellar pearlite	1425	40	6

Thus, the critical cooling rate was identical (700 degrees Fahr. per second) for average austenitic grain-sizes from 130 to 40 grains per square inch at 100 diameters magnification (grain-size number 8 to 6). This circumstance is probably to be attributed to differences in the amount and distribution of carbon in the austenite. Based on the recognized effect of grain-size alone, a lower critical cooling rate might be anticipated for the specimen containing 40 austenitic grains per square inch at 100 diameters magnification as compared with specimens of the same steel having 100 or 130 grains per square inch at 100 diameters magnification. When the specimen of initially coarse pearlitic structure is heated to 1425 degrees Fahr. (775 degrees Cent.) it is a relatively short distance above the eutectoid temperature, a limited proportion of the cementite goes into solution, a considerable number of free cementite particles remain within the austenite grains and a network of cementite outlines the grains (Fig. 7C). Both the relatively low carbon content of the austenite and the presence of a considerable number of free cementite particles within the grain supplying nuclei for austenite decomposition in the Ar′ temperature range, act to increase the critical cooling rate and oppose the effect of the relatively large grain, which decreases the critical cooling rate. The resultant rate has thus become the same as that of the much finer-grained specimen heated from an ini-

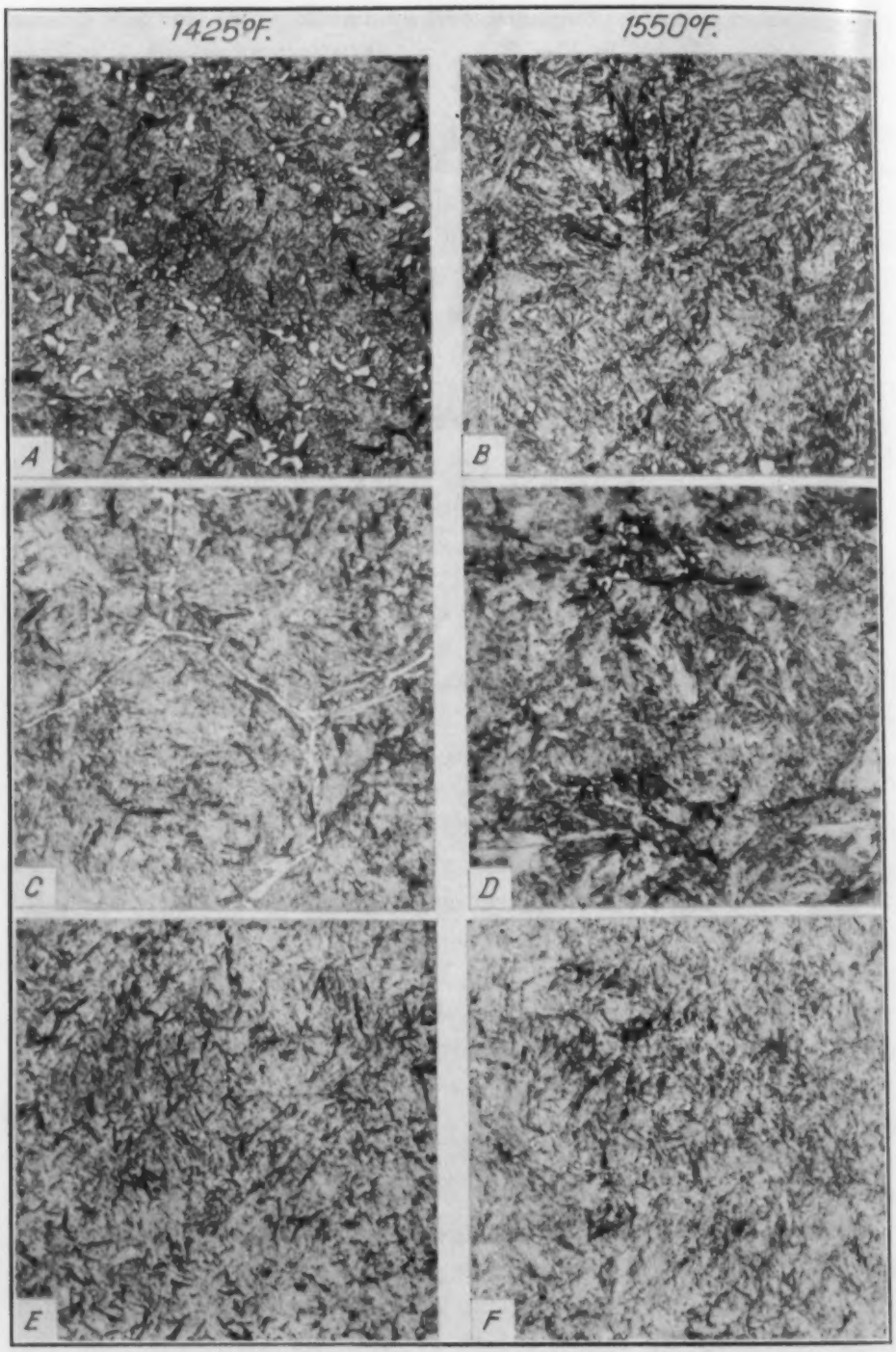


Fig. 7—Effects of Initial Structure on the Free Carbides Remaining in Specimens of Steel 65 Quenched from 1425 and 1550 Degrees Fahr. (775 and 845 Degrees Cent.). A and B, Initial Structure Spheroidized Cementite. C and D, Initial Structure Coarse Pearlite. E and F, Initial Structure Fine Pearlite or Sorbite. Etched in 1 Per Cent Nitric Acid in Alcohol. × 500.

tial sorbitic structure to 1570 degrees Fahr. (855 degrees Cent.), where the carbon content of the austenite is higher than in the first specimen and where less free cementite remains (Fig. 7F). Both these factors act to decrease the critical rate in opposition to the increased rate indicated by the smaller grain-size.

The initially spheroidized specimen of steel 65 has a grain-size at 1475 degrees Fahr. (800 degrees Cent.) slightly smaller than the initially sorbitic specimen at 1570 degrees Fahr. (855 degrees Cent.), and should give a relatively higher critical cooling rate. This specimen also should have an austenite of somewhat lower carbon content, tending to increase further the critical cooling rate. Yet actually the observed rate was again 700 degrees Fahr. (370 degrees Cent.) per second. The factor which probably offsets any such increase in critical rate is a difference in the number of free cementite particles remaining in the austenite grain at the moment of quenching. The initially spheroidized specimen quenched from 1475 degrees Fahr. (800 degrees Cent.) contained a relatively small number of rather coarse cementite particles (a structure intermediate between Fig. 7A and Fig. 7B), while initially sorbitic specimens quenched from 1550 to 1570 degrees Fahr. (845 to 855 degrees Cent.) may contain a great number of very small cementite particles. The relatively small number of coarse cementite particles is less effective in providing nuclei for the transformation of austenite, in the Ar′ temperature range, and this may have acted to oppose the tendency of the smaller grain to increase the critical cooling rate of the initially spheroidized specimen.

It should be pointed out, however, that the critical cooling rate of the initially sorbitized steel decreased very rapidly with increase in quenching temperature from about 1550 to 1625 degrees Fahr. (845 to 885 degrees Cent.) (Fig. 4), and the austenite grain-size showed a marked increase with increase in temperature from 1550 to 1625 degrees Fahr. (845 to 885 degrees Cent.) (Fig. 3) so that precise estimates of these properties for a temperature of 1570 degrees Fahr. (855 degrees Cent.) became difficult. That is, a small change in temperature in the neighborhood of 1570 degrees Fahr. (855 degrees Cent.) materially changes both the critical cooling rate and the austenitic grain-size of the initially sorbitized steel.

The curves of Fig. 6 show little evidence of an effect of initial structure in steel 65 when the critical cooling rates are 300 degrees Fahr. (150 degrees Cent.) per second and less. These rates corre-

spond to quenching temperatures of 1600 degrees Fahr. (870 degrees Cent.) or more, temperatures at which all the cementite is in solution.

The effect of the carbon content of an austenite of a given grain-size on the critical cooling rate is illustrated by curve "X" of Fig. 6. The data for this curve were obtained in the following manner. Specimens of steel 65 were heated to temperatures from 1600 to 1800 degrees Fahr. (870 to 980 degrees Cent.) to establish the characteristic grain-size, were then cooled slowly to 1400 degrees Fahr. (760 degrees Cent.), held at that temperature for 30 minutes and quenched to determine the critical cooling rates. The cooling from the temperature establishing the grain-size to 1400 degrees Fahr. (760 degrees Cent.) was sufficiently slow to permit practically all of the cementite which precipitated to collect as grain boundary network. The resulting specimens, therefore, had the range of austenitic grain-sizes shown in Fig. 6 but the austenite grains regardless of size were of the same carbon content and this carbon content was less than that of the austenite grains of the same size quenched directly from the grain coarsening temperatures. The increase of the critical cooling rate for a given size of austenite grain caused by a lower carbon content of the austenite is very marked.

As has already been shown in Figs. 3 and 4 both austenitic grain-sizes and critical cooling rates for temperatures between 1425 and 1775 degrees Fahr. (775 and 970 degrees Cent.) cover appreciably narrower ranges for the controlled grain-size steel 68 than for the non-controlled steel 65. Steel 68 with an initial structure of coarse pearlite covers a range of critical cooling rates from 700 to 350 degrees Fahr. (370 to 175 degrees Cent.) per second with no change in austenitic grain-size. This holds true not only for the range of quenching temperatures below the A_{cm} temperature, where differences in the amount and uniformity of distribution of carbon dissolved in the austenite may affect changes in critical cooling rates, but also is true for quenching temperatures considerably above the A_{cm} temperature, where such effects of carbon from cementite should be absent. In this higher range of quenching temperature, if the grain-size is constant and the effects of the amount and distribution of carbon from cementite are absent, changes in critical cooling rates must be dependent on some other factor, probably the nucleation effects of the oxides or carbides which are commonly considered to be the influencing elements in controlling austenitic grain-sizes.

Steel 68 with an initially spheroidized structure shows a very similar wide range of critical cooling rates with constant austenitic grain-size, both in the range of high and of low critical cooling rates, rates corresponding to low and high quenching temperatures, respectively. There is, however, a marked difference in grain-size between the two quenching temperature ranges. But within a rather broad range of quenching temperature above the A_{cm} temperature, where carbon content and distribution should be of little or no effect, the critical cooling rate changes markedly. This is quite parallel to the behavior just discussed for this steel with an initial coarse pearlitic structure. The wide range of cooling rates for steel 68 of initial sorbitic structure, in spite of the relatively slight change in grain-size, may be tentatively explained in a similar manner.

The continued change of critical cooling rates above the A_{cm} temperature, with constant grain-size and no effect to be expected from carbon content, is an indication that oxide and carbide grain-control constituents may themselves be undergoing modification as the quenching temperature increases. Such modifications are in the direction of decreasing the effectiveness of such particles as nucleation centers for austenite decomposition, as evidenced by the fact that the critical cooling rates become progressively lower.

Summary

Two commercial 1 per cent carbon tool steels were selected, on the basis of widely different hardening characteristics, for a detailed study of the relation of the initial structure, prior to heating for hardening, on the austenitic grain-size and grain-growth characteristics. Austenitic grain-size measurements were made and critical cooling rates were determined for the temperature range from 1425 to 1775 degrees Fahr. (775 to 970 degrees Cent.).

The data thus secured permitted the derivation of grain-size —critical cooling rate relations throughout this range of temperature.

For quenching temperatures below that at which all the carbon is completely dissolved in the austenite, both austenitic grain-size and critical cooling rates are influenced to a large degree by the initial structure of the steels. Above this temperature each steel approached both a grain-size and a critical cooling rate which was characteristic of the steel regardless of its initial structure.

At the highest temperature, namely 1775 degrees Fahr. (970

degrees Cent.), the characteristic grain-size was smaller and the characteristic critical cooling rate was higher for the steel known to have been made under conditions producing so-called controlled grain-size steel.

In the correlation of austenitic grain-size with critical cooling rates the noncontrolled grain-size steel showed a marked effect of grain-size throughout the entire range of quenching temperatures. The influence of the initial structure was also evident at the lower quenching temperatures.

The critical cooling rate of the controlled grain-size steel changed very appreciably with little or no change in austenitic grain-size. At the lower quenching temperatures difference in carbon content and carbon distribution in the austenite may be the controlling factors, but at higher temperatures oxides or carbides introduced for grain control are probably the effective factors in changing the critical cooling rate.

The initial structure of the controlled grain-size steel exerts an influence on the grain-size–critical cooling rate relations at both low and high quenching temperatures.

A few determinations made on a noncontrolled grain-size steel indicated that the critical cooling rate of this steel with austenitic grains containing carbon above eutectoid composition is lower than that for the same steel with grains of the same size containing about eutectoid proportions of carbon.

DISCUSSION

Written Discussion: By R. Schempp, metallurgist, Halcomb Steel Co., Syracuse, N. Y.

The authors have my heartiest congratulations for the excellence and timeliness of their paper, dealing with the hardening characteristics of carbon tool steels. The question of tool steels has received a great deal of attention lately and any information on this subject is studied very attentively and with a great deal of appreciation.

Since the importance of this paper is so great, I should like to present some of the results that we have obtained in our laboratories at the Halcomb Steel Co. "Grain-size control" and "inherent characteristics" are two widely used phrases today. The prevailing idea is that steel has certain characteristics "inherently" and will react similarly in all conditions when heat treated from the same temperatures. This point of view, generally believed, is not true as the final product is influenced by many factors.

First, controlled grain-size steel implies the addition of inhibitors in suf-

ficient quantities to prevent grain growth at elevated temperatures. This implication, grain-size control, is not only a function of chemical composition but also of the melting practice, teeming, the rate of solidification, and once solidified, these factors help to determine the inherent characteristics at the various temperatures; while prior structure, hot and cold working, and soaking time influence the final result. Chemical composition indicates only the amount of certain elements in the material by weight, and does not identify their size, form, or stability at the various temperature ranges. If sufficient inhibitors are added to the metal, grain growth is controlled within certain temperature limits, and two heats, with identical chemical composition, may behave exactly alike at the lower temperatures and may respond differently with the further application of heat, while another series of heats will behave oppositely at the lower extremes and similarly at the higher temperatures. This variation while basically a function of the inherent properties of the metal, is markedly influenced by the condition of the grain prior to final hardening.

In general it may be said that a fine-grained initial structure, when heated for a corresponding length of time, an initially coarse-grained material will form a finer-grained austenitic structure than the latter. This is very marked at the lower temperatures, until the coarsening range is reached and then, the steel responds inherently. But neglecting this characteristic, grain growth continues with temperature and soon the fine-grained material becomes coarser than the original coarse grain, due to its greater rapidity of growth. As grain growth is a function of time-temperature, the temperature at which this may occur is determined by time, and this may occur in some heats either after two hours at 1900 degrees Fahr. (1035 degrees Cent.) or about 10 minutes at 2350 degrees Fahr. (1290 degrees Cent.).

The effect of prior heating may be briefly summed up by saying that rapid cooling causes a fine grain material, which on subsequent heating to temperatures above the critical, will grow more rapidly than the coarser, slowly cooled material. At first, at the lower temperature, the latter, coarse grain is deeper hardening and has a greater depth of penetration, but as soon as the coarsening temperature is reached, the values are practically the same, and at still higher temperatures, the fine-grained material becomes the deeper hardening with a greater depth of penetration than the coarse.

Another major factor which influences the inherent properties of tool steel is the effect of working. Hot or cold work is usually not entirely removed on subsequent heating, and will therefore influence, often very markedly, the final results of hardened material.

Cold work distorts the grain causing a fine crystalline aggregate which, on heating to the gamma range, grows much faster than unworked or less strained material. The effect of hot working is regulated mainly by the finishing temperature and the amount of reduction. The lower the finishing temperature, the finer is the grain-size. The greater the amount of reduction, the finer is the grain-size, and consequently the result:—a smaller initial austenitic grain, but a coarser one at the higher temperatures.

The authors are certainly to be complimented again on their thought-provoking paper and we hope that they will present others in the near future on this vital subject.

Written Discussion: By T. E. Hamill and Lieutenant Commander A. J. Wellings of the Naval Gun Factory, Washington, D. C.

This interesting paper gives us further light on why certain 1 per cent carbon steels show such large variation in depth of hardening and hence physical properties. Bain and Shepherd have shown us that the prior or prehardening structure of high carbon steels has a pronounced effect on the austenitic grain-size and depth of hardening, but it appears to be shown even more clearly here. This paper proves that the amount and size of the free carbides have a definite effect on the austenitic grain-size and critical cooling rate in the noncontrolled grain-size steel. In the controlled grain-size steel, at temperatures below 1550 degrees Fahr. (845 degrees Cent.), the alumina or aluminum appears to be more effective in increasing the critical cooling rate than it does controlling the austenitic grain-size. Above 1600 degrees Fahr. (870 degrees Cent.), where all of the carbides are in solution, the alumina (or aluminum) appears to be effective in controlling both the austenitic grain-size and the critical cooling rate.

There are a few questions which I would like to ask. In Fig. 3, the curves obtained on steels 68A and 65B have practically the same austenitic grain-size at 1425 degrees Fahr. (775 degrees Cent.) but change at different rates with increase in quenching temperature. Would it not be expected that the larger spheroidized carbides of steel 65 would prevent grain growth much more than the submicroscopic carbides of the sorbite of steel 68 even with the alumina?

The critical cooling rate-temperature curve (Fig. 4) obtained with steel 65A between 1425 and 1550 degrees Fahr. (775-845 degrees Cent.) appears to be difficult to explain. The austenitic grain-size at 1550 degrees Fahr. (845 degrees Cent.) is twice as large as it is at 1425 degrees Fahr. (775 degrees Cent.) and in addition has more carbides in solution and hence less free carbides. Under such conditions, would it not be expected that the increased carbon content of the austenite and smaller amount of free carbides would tend to lower the critical cooling rate?

The example given in Fig. 5 checks the critical cooling rate curves given in Fig. 4, but it would be desirable to see a few more practical examples given. For instance, a comparison between steel 65A quenched from 1575 and 1600 degrees Fahr. (855-870 degrees Cent.) and between steel 68C quenched from 1725 degrees Fahr. (940 degrees Cent.) and steel 68B quenched from 1800 degrees Fahr. (980 degrees Cent.).

Fig. 6 shows that steels 65A, 65B, 68B and 68C have an austenitic grain-size of approximately 45 grains per square inch and a critical cooling rate of 400 degrees Fahr. per second. Can it be assumed that these steels, under such conditions, will have the same physical properties? Such a check would be interesting.

In Fig. 6, the authors state that curve "X" shows the increase of the critical cooling rate for a given-size austenite grain caused by a lower carbon content of the austenite, is very marked. Is it to be inferred from this that the cementite which has precipitated and collected around the grain boundaries has no effect on the critical cooling rate? If so, does this not mean that carbon steels of eutectoid composition will have a higher critical cooling rate than the hypereutectoid carbon steels? The results obtained at the Bureau of Standards

some time ago and other investigators have shown just the opposite, i.e., carbon steels, of eutectoid composition, have a lower critical cooling rate than the hypereutectoid steels. Curve "X" also shows that even though the grain-size of the austenite is varied from 25 to 4 grains per square inch, the critical cooling rate will not be affected appreciably if the carbon content of the austenite does not change.

Oral Discussion

G. V. LUERSSEN:[1] This paper will be greatly appreciated by those who have worked on the problem of hardenability, since it helps to explain many of the characteristics of tool steels observed through the practical routine methods of test now regularly employed. A mere reading of the paper does not serve to convey the tremendous amount of laboratory work involved in compiling the rate curves, and the authors are to be commended upon the evident care and thoroughness with which this work was conducted.

Referring to Fig. 3, it will be seen that in the initially spheroidized condition the controlled steel, No. 68, is stable with regard to grain-size up to a quenching temperature of 1550 degrees Fahr. (845 degrees Cent.), while the noncontrolled steel, No. 65, coarsens with increasing quenching temperatures. Similarly, referring to Fig. 4 the controlled steel shows greater stability with regard to critical quenching rate, or in other words penetration. The average consumer of tool steel is interested in its behavior from the initially spheroidized condition, this being the structure regularly supplied for the reason that it is best adapted to general usage conditions. The curves consequently show clearly the advantage of the controlled steels as currently supplied the trade, from the standpoint of both wider quenching range, and more uniform penetration.

The paper further confirms the conception now generally accepted of two factors influencing behavior, namely the carbide effect and the inherent effect. In the controlled steel the inherent effect is predominant, overshadowing the carbide effect. In the noncontrolled steel on the other hand the carbide effect is quite strong, governing to a large extent the behavior of the steel in the quenching ranges in which excess carbide is going into solution. It is hoped that further work in prospect by the authors will uncover additional information with regard to these two effects.

Authors' Closure

We are certainly appreciative of the several discussions of our paper. Messrs. Hamill and Wellings have propounded several questions in their comments. Replying to these, in order:—We would not expect the larger spheroidized particles in the initially spheroidized specimens of steel 65 necessarily to be more effective in preventing austenitic grain growth than the finer particles in the initially sorbitic specimens of steel 68. The greater number and wider distribution of the smaller particles should be more effective in this respect than the presence of a smaller number of very large particles. The comments of Messrs. Hamill and Wellings on Figs. 4 and 6 are indeed interesting.

[1]Metallurgist, Carpenter Steel Co., Reading, Pa.

Increasing the carbon content of the austenite would, indeed, be expected to decrease the critical cooling rate (other controlling factors remaining constant). However, increasing the quenching temperature from 1425 to 1550 degrees Fahr. (775-845 degrees Cent.) of the initially sorbitic specimens of steel 65 may not have materially changed the number of the free carbide particles in the quenched specimens. The fact that both specimens actually had the same critical cooling rate, was further confirmed by the depth of hardening of ¾-inch round specimens. Increasing the carbon content of the austenite, in the example cited, does not necessarily mean fewer free carbide particles, it simply means slightly more carbon in solution and less carbon as precipitated carbides. Earlier work carried out at the National Bureau of Standards and by other investigators on the critical cooling rates of plain carbon steels as dependent on the carbon content of the steel was done without due regard to the simultaneous influence of austenitic grain-size. While we do not wish to infer too much from the limited number of tests represented in Fig. 6 by curve X, the results do indicate that the carbon content of the austenite has a pronounced influence on the critical cooling rate. Furthermore, these data suggest the possibility of a hypereutectoid steel having a lower critical cooling rate than either a eutectoid or hypoeutectoid steel, provided the austenitic grain for each steel is of the same size and the quenching temperatures establishing the grain-size are sufficiently high to have all the carbon in solution. We are now working on this very problem in an attempt to determine whether or not the austenitic grain-size influenced the results of previous investigations on the effects of carbon on the critical cooling rate.

Two steels of the same composition and of the same austenitic grain-size and critical cooling rate may have different physical properties after identical heat treatments. However, if the additional condition is imposed that the austenitic grains shall be of the same composition and constitution, the steels should have the same physical properties.

INTERPRETATION OF TORSION IMPACT PROPERTIES OF CARBON TOOL STEEL

By G. V. Luerssen and O. V. Greene

Abstract

The paper discusses the characteristic torsion impact curve on quenched and drawn tool steel presented by the authors in previous papers. It is the purpose of the paper to show that the peculiarities of this curve can be explained by the structural and physical changes occurring in the drawing operation. Particular reference is made to the drop in impact resistance between drawing temperatures of approximately 350 and 450 degrees Fahr. (175-230 degrees Cent.) on the plain carbon steels. It is shown that this drop in impact is accompanied by a drop in ductility, and by means of reconstructed impact curves calculated from hardness and ductility measurements, this decrease in ductility is proven definitely to account for the drop in impact value.

Correlation is then made between impact resistance and thermal, X-ray and volume change data, and it is shown that the drop in ductility, and consequently in impact value is caused by a structural change involving the decomposition of austenite. Direct comparisons are then made between torsion impact curve and length change and magnetic curves. Comparisons are also made between impact curves plotted from quenched and drawn specimens, and from specimens quenched, cooled in liquid air and drawn, from which it is concluded that the first, or rising stage of the curve is the result of stress relief in the quenched martensite, the second or falling stage is caused by breakdown of retained austenite to the less ductile martensite, and the third or rising stage results from the gradual breakdown of martensite into the softer more ductile constituents.

Introduction

IN two previous papers (1), (2),[1] dealing with the application of the torsion impact test to hardened steel, the writers have pre-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The authors, G. V. Luerssen and O. V. Greene, are members of the Metallurgical Department, Carpenter Steel Co., Reading, Pa. Manuscript received June 1, 1935.

sented data which show a peak in the impact resistance curve at a relatively low drawing temperature, viz., 350-400 degrees Fahr. (175-205 degrees Cent.) followed by a valley at a somewhat higher draw, viz., 450-500 degrees Fahr. (230-260 degrees Cent.). A characteristic curve for 1.00 per cent carbon steel quenched in brine at 1450 degrees Fahr. (790 degrees Cent.), in which impact resistance is plotted against drawing temperature, is shown in Fig. 1. In general

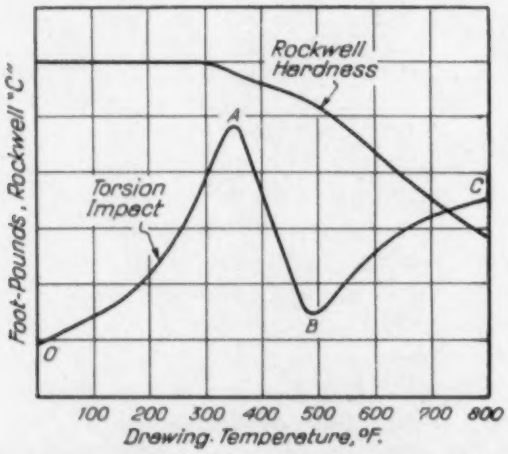


Fig. 1—Characteristic Torsion Impact and Rockwell Hardness Curves for Carbon Tool Steel Quenched at 1450 Degrees Fahr. (790 Degrees Cent.) and Drawn.

form this curve is typical of the results on many types of carbon and low alloy tool steels varying upward from 0.60 per cent carbon, the exact lateral position of the peak and valley depending upon the quenching temperature applied.

The peak of impact at A, and the decrease in toughness as indicated by the drop in the curve from point A to the point B are sharply at variance with the time honored belief that the toughness of a hardened tool steel increases steadily with increasing drawing temperature. Consequently there appears to be need for interpretation of the behavior of this curve in terms of more fundamental properties of the steel. This paper seeks to provide such an interpretation, particularly of the behavior between the points A and B, by examining the physical changes through the range in question.

Before entering upon a study of these changes it will be advisable first to briefly review the torsion impact test and the mechanics involved. The specimen consists in a bar having an over-all length of approximately 4¾ inches, the ends measuring ½ inch square. The

test length is exactly 1 inch between fillets and the diameter is ¼ inch. The test is made by properly chucking this test specimen so that it can be broken suddenly in torsion and the absorbed energy accurately measured. The details of this test have already been described (1), and need not be reported here. Since the test specimen is of uniform section, the notch effect may be disregarded entirely and the mechanics of the test become relatively simple. The energy or work expended by the impact machine in breaking a specimen is a force multiplied by the distance through which this force acts, and is expressed as foot-pounds. Similarly the resistance to rupture offered by the specimen itself is the product of two components, namely the strength of the material and its ductility, the first indicating the force necessary to deform the material, and the second the distance through which the force acts in completely rupturing the bar. This product we term toughness. Since strength is roughly proportional to hardness, and since Rockwell hardness is found to decrease in a fairly smooth curve with increased drawing temperatures, it is obvious that the component of strength is not the controlling factor influencing the irregular behavior of the impact curve. Emmons (11) in the development of his toughness coefficient by the static torsion method also brought out this point. In view of this fact it appeared that a study of ductility would probably yield an explanation both of the peak of the impact curve and of the underlying reasons for this peak.

Study of Ductility

All of the work reported in this paper was conducted upon a heat of carbon tool steel of the following analysis:

	Per Cent
Carbon	1.08
Manganese	0.26
Silicon	0.27
Phosphorus	0.014
Sulphur	0.014

The hardening procedure in all cases was as follows: Specimens were preheated to 800 degrees Fahr. (425 degrees Cent.) in an electric muffle, transferred to a lead pot at the quenching temperature, held for exactly 3 minutes in the lead and quenched.

Three lots of impact specimens were made up, each lot containing twenty-six pieces. One lot was quenched in brine at 1450

degrees Fahr. (790 degrees Cent.), the second at 1550 degrees Fahr. (845 degrees Cent.), and the third at 1600 degrees Fahr. (870 degrees Cent.). Duplicate pairs from each lot were drawn for one hour at twelve different temperatures ranging from 300 to 800 degrees Fahr. (150-425 degrees Cent.), and one pair was left in the undrawn condition. Before testing, a straight line was scribed along the test length of each specimen, and one face of the square test ends was accurately surface ground so that both faces were in exactly the same plane. All specimens were broken in the torsion impact machine, after which they were assembled and the angle of permanent twist determined by measuring the angle between the two ground surfaces. In general only the specimens drawn higher than a temperature of 350 degrees Fahr. (175 degrees Cent.) could be assembled due to the extreme shattering at the lower drawing temperatures. The torsion impact values and the angles of permanent twist are given in Fig. 2, in which the average of two duplicate tests was plotted in each case. The maximum divergence between duplicates was 12 per cent for the impact values, and 15 per cent for the angle of twist. Fig. 3 shows a set of impact specimens for each of the three quenching temperatures after having been broken and assembled, the scribe mark showing the amount of permanent twist.

The drop in ductility from the drawing temperature corresponding to the peak of the impact curve, to that corresponding to the valley of the impact curve is quite striking, and there appears to be no doubt that this drop in ductility accounts for the characteristic drop in the curve from a draw of approximately 350 degrees Fahr. (175 degrees Cent.) to a draw of approximately 450 degrees Fahr. (230 degrees Cent.).

To carry this study a step farther an attempt was made to reconstruct the torsion impact curve by calculating absorbed energy from the hardness data and angle of twist. Since no accurate data are available on the shearing strength of extremely hard steels it was necessary to make a somewhat broad assumption, namely that shearing strength is approximately equal to tensile strength. Guillet and Portevin (9) as well as one of the authors (10) have found the tensile strength of hard steels expressed in pounds per square inch, to be approximately 500 times the Brinell hardness number. Shearing strength expressed in pounds per square inch was consequently assumed to be 500 times the Brinell hardness value, or approximately 5000 times the Rockwell "C" value. Two other assumptions were

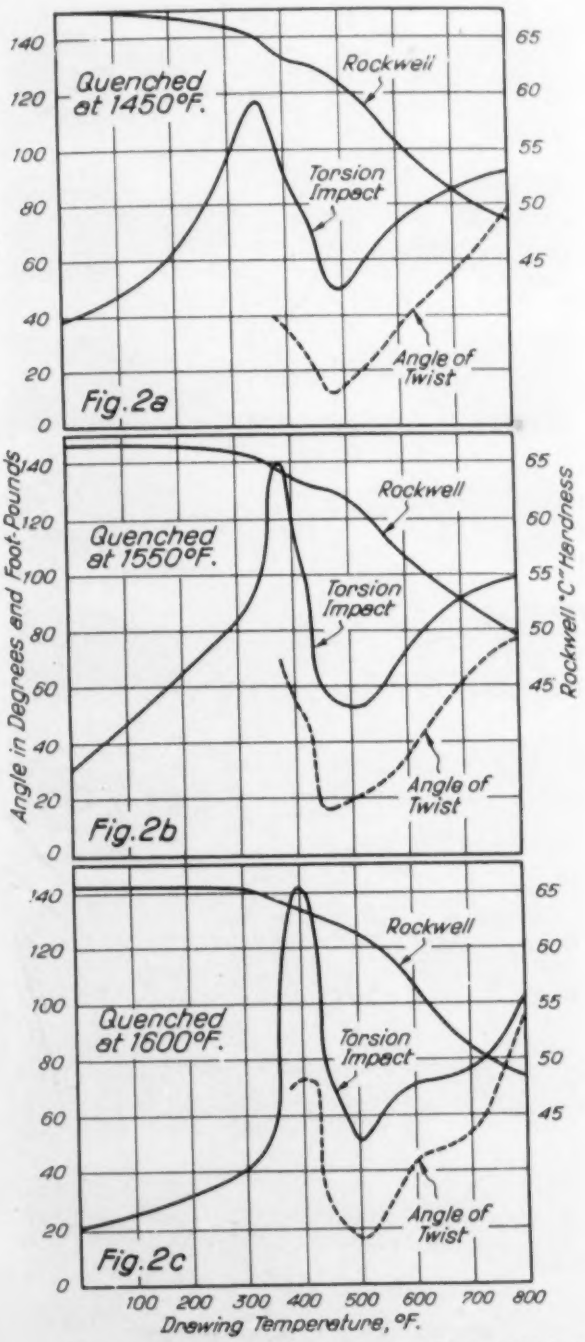


Fig. 2—Comparisons of Torsion Impact Values and Angle of Permanent Twist on 1.08 Per Cent Carbon Tool Steel Brine-Quenched at Three Different Temperatures and Drawn.

made, first, that forces acting upon the piece during plastic deformation are opposed by a constant resistance to rupture equal to the

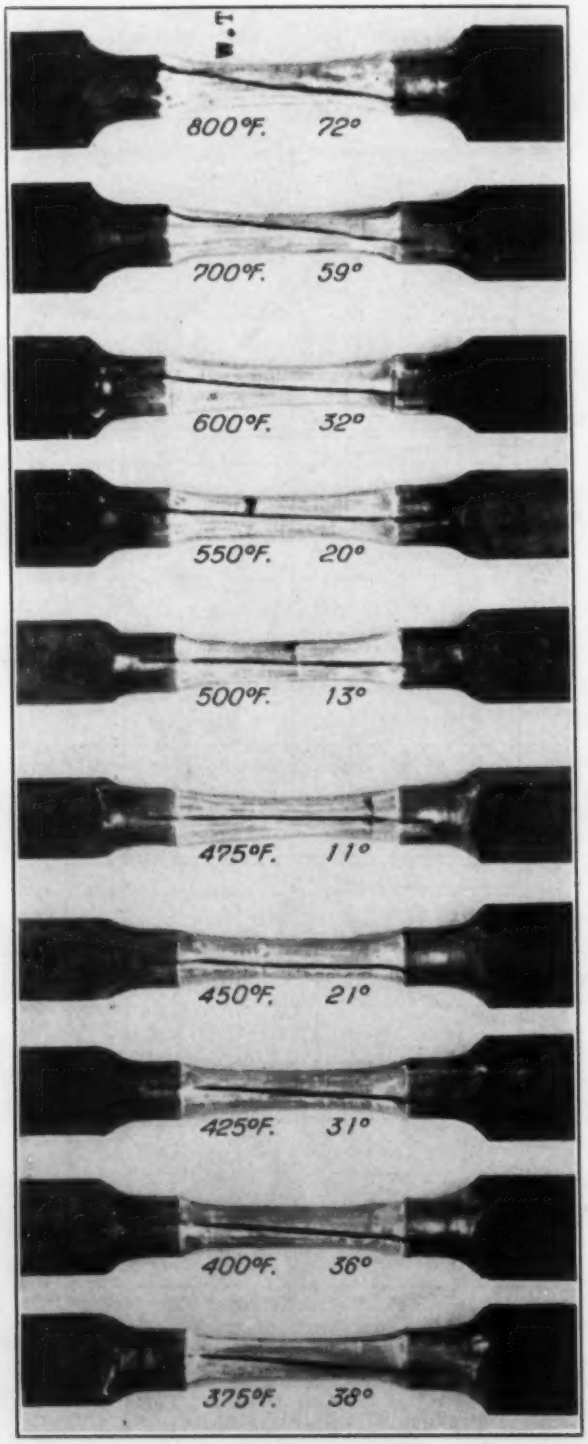


Fig. 3a—Brine-Quenched from 1450 Degrees Fahr. (790 Degrees Cent.) Drawn for 1 Hour at Temperatures Shown. Second Set of Figures Show Angle of Permanent Twist.

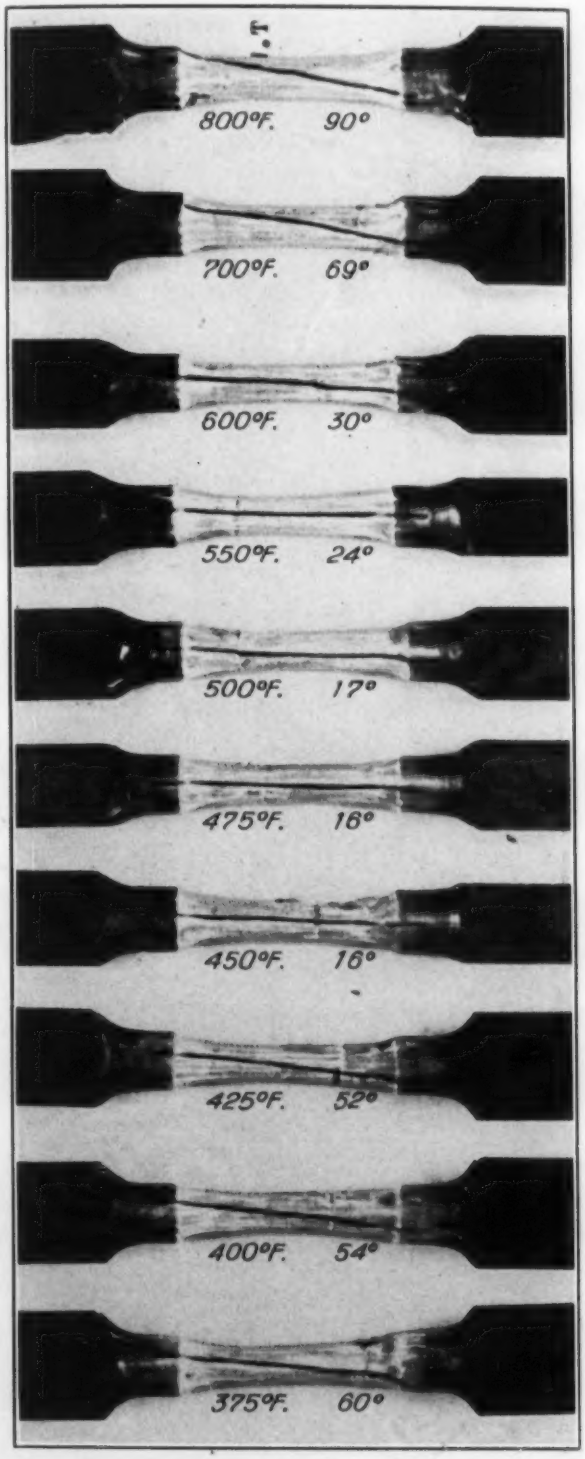


Fig. 3b—Brine-Quenched from 1550 Degrees Fahr. (845 Degrees Cent.) Drawn for 1 Hour at Temperatures Shown. Second Set of Figures Show Angle of Permanent Twist.

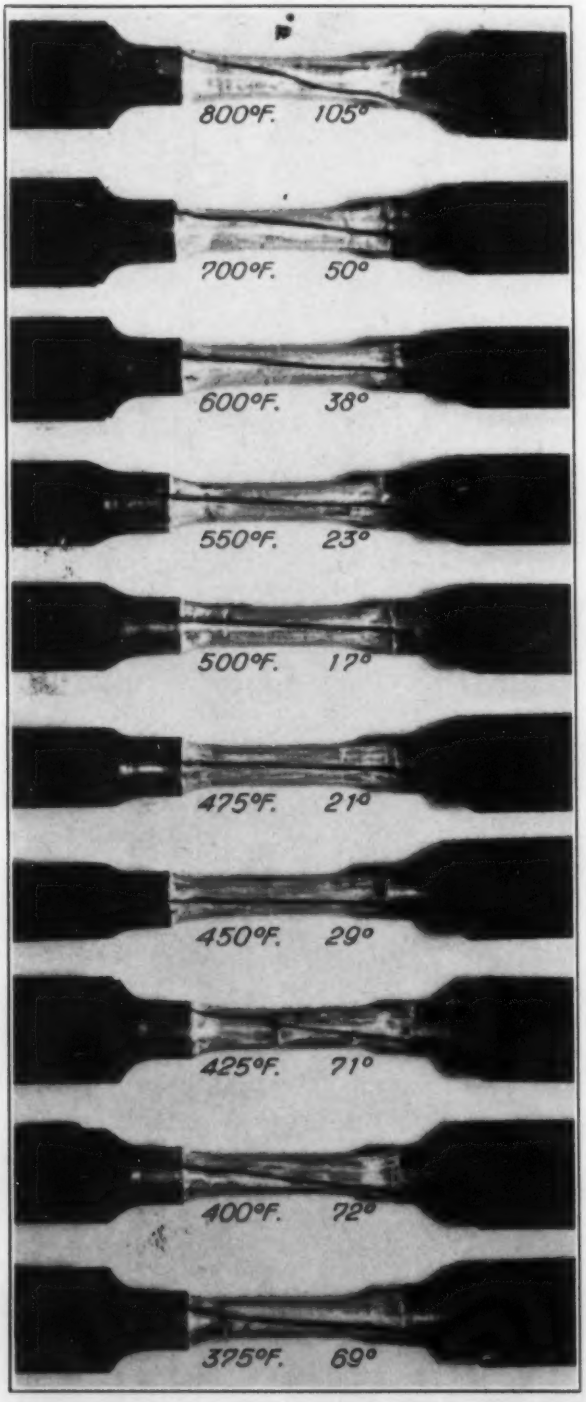


Fig. 3c—Brine-Quenched from 1600 Degrees Fahr. (870 Degrees Cent.) Drawn for 1 Hour at Temperatures Shown. Second Set of Figures Show Angle of Permanent Twist.

shearing strength, and second, that the ultimate shearing strength in hardened steels is close to the elastic limit. While these assumptions probably take some liberties it is believed that they are sufficiently close to the truth to serve the present purpose.

The details of the mathematical development are given in the appendix. The total work expended in breaking the piece will be the sum of W_1, the work of elastically deforming the specimen up to the elastic limit, and W_2 the work expended in actually rupturing the specimen after the elastic limit is passed. $W_1 = 0.167 \times 10^{-9}\ S$ in which S is the ultimate shearing strength. $W_2 = \frac{aS}{158800}$ in which a is the permanent angle of twist. Combining these two formulas $W = S(0.629 \times 10^{-5}a + 0.169 \times 10^{-9}S)$.

Calculated curves based on the data shown in Fig. 2 are given in Fig. 4.

The similarity of the experimental and calculated curves both qualitatively and quantitatively is quite interesting, and proves conclusively that the drop in impact value from the peak of the valley is caused by a decrease in the angle of permanent twist. It now remains to examine the causes underlying this decrease in ductility.

Correlation of Torsion Impact With Other Physical Properties

There have been numerous studies made of the behavior of hardened high carbon steels during drawing, notably by Maurer (8) and Scott (3) who investigated volume change; Heindlhofer and Wright (4) and Kurdyumov (5) who used X-ray methods; de-Forest (6) who employed magnetic methods; and Scott and Movius (7) who have studied the thermal behavior and correlated this with volume change. None of these studies to our knowledge has ever been correlated with impact resistance. It is interesting therefore briefly to review the results of the foregoing investigators in light of the torsion impact curve.

Volume Change: Maurer (8) and Scott (3) both found that upon tempering a quenched high carbon steel, the volume decreased up to a tempering temperature of approximately 350 degrees Fahr. (175 degrees Cent.) at which point there was a sharp reversal followed by expansion up to approximately 450 degrees Fahr. (230

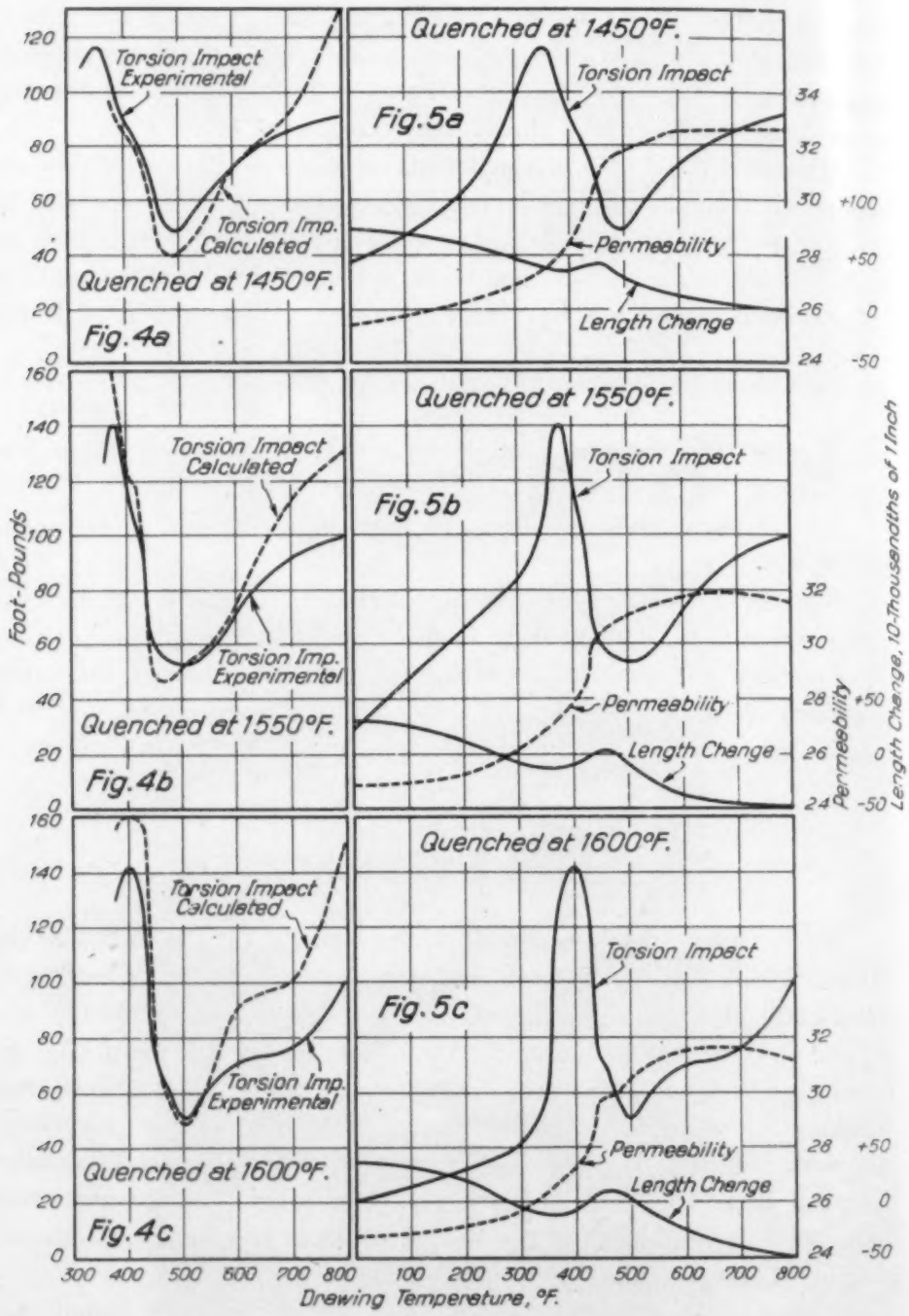


Fig. 4—Comparison of Torsion Impact Curve with Curve Calculated from Rockwell Hardness and Angle of Twist on a 1.08 Per Cent Carbon Tool Steel Brine-Quenched at Three Temperatures and Drawn.

Fig. 5—Correlation of Torsion Impact Values with Magnetic Permeability and Length Change on a 1.08 Per Cent Carbon Tool Steel Brine-Quenched at Three Temperatures and Drawn.

degrees Cent.) at which point a second reversal occurred and the volume again decreased with increasing tempering temperatures. These results have been confirmed many times, and it is now generally accepted that the expansion phenomenon between 350 and 450 degrees Fahr. (175-230 degrees Cent.) is caused by transformation of the retained austenite to martensite.

Thermal Change: Scott and Movius (7) on a 0.95 per cent carbon steel quenched in water and slowly heated, found a heat evolution starting at approximately 330 degrees Fahr. (165 degrees Cent.), coming to a maximum at about 500 degrees Fahr. (260 degrees Cent.), corresponding closely to the range of austenite transformation already discussed.

X-Ray Evidence: Heindlhofer and Wright (6) show that on a ball steel containing 1.06 per cent carbon and 0.71 per cent chromium, upon water quenching at 1685 degrees Fahr. (920 degrees Cent.) and drawing, austenite disappears between 390 and 490 degrees Fahr. (200-255 degrees Cent.). They found this austenite breakdown to be accompanied by expansion. Kurdyumov (5) in a very interesting X-ray study, shows upon a 1.40 per cent carbon water-quenched steel, the disappearance of tetragonal lattice at a temperature of 257 degrees Fahr. (125 degrees Cent.) and complete disappearance of retained austenite at 480 degrees Fahr. (250 degrees Cent.).

From the above studies it appears that the structure of a quenched high carbon steel consists of a mixture of martensite of a distorted or tetragonal lattice, and retained austenite. Drawing or tempering proceeds in three separate and distinct stages with increasing temperature, first stress relief, second austenite transformation accompanied by some coalescence of carbide in the martensite originally formed, and third the gradual coalescence of carbide to form troostite. Heating to approximately 300 degrees Fahr. (150 degrees Cent.) results in stress relief, the martensite assuming a true cubic form, as indicated by the disappearance of doublets on the X-ray spectrum. Through this range the torsion impact curve rises to reach a peak at from 350 to 400 degrees Fahr. (175-205 degrees Cent.). This range is further characterized by shattered fractures, indicating highly stressed material.

It appears to be established next that transformation of retained austenite to martensite begins at temperatures from 330 to 395 degrees Fahr. (165-200 degrees Cent.) and ends between 450 and 500 degrees Fahr. (230-260 degrees Cent.). It is interesting to note

how closely the above data agree with the impact and ductility curves shown in Fig. 2. The peaks of these curves occur at drawing temperatures ranging from 350 to 400 degrees Fahr. (175-205 degrees Cent.), and the valleys from 475 to 500 degrees Fahr. (245-260 degrees Cent.) depending upon quenching temperature.

The third stage starts at 450 to 500 degrees Fahr. (230-260 degrees Cent.), at which point the martensite gradually changes to troostite, and later to sorbite with ascending temperatures, accompanied by a gradual rise in the impact resistance curve.

Since the volume change test appears to be one of the most reliable in detecting the behavior of retained austenite in the second stage, it was decided to carry through a series of length change tests with each of the impact series shown in Fig. 2. In addition to this three similar series of pieces for magnetic test were included. Both the magnetic pieces and the length change specimens measured ¼ inch diameter by 3 inches in length, this size being selected to duplicate as nearly as possible the impact test section. The volume change specimens were ground flat on the ends to allow accurate length measurements. In order to duplicate as nearly as possible the structural condition of the impact bar, each series was heated in the same lead pot and quenched at the same time at its corresponding impact series.

The length change specimens were carefully gaged for length in the soft condition, and this length was taken as the zero point to which later measurements were referred. Immediately after quenching, several specimens were again gaged, allowed to rest, and then measured periodically until contraction ceased, and the length became permanent. This was found to require 48 hours, and all specimens were consequently allowed to rest for this length of time before gaging for the "as-quenched" length. Specimens were drawn and gaged at each temperature in quintuplicate. The micrometer used read to 0.0001 inch, and the average of four readings on each specimen taken 90 degrees apart was recorded.

The magnetic tests were made by Dr. A. V. deForest by a method (6) which determines permeability, values being expressed in arbitrary units. Results of length change and magnetic tests compared with the impact curves are shown in Fig. 5. It will be seen that the drop in impact from peak to valley corresponds quite closely to austenite breakdown as indicated both by expansion on the volume curve, and increase in permeability on the magnetic curve. Com-

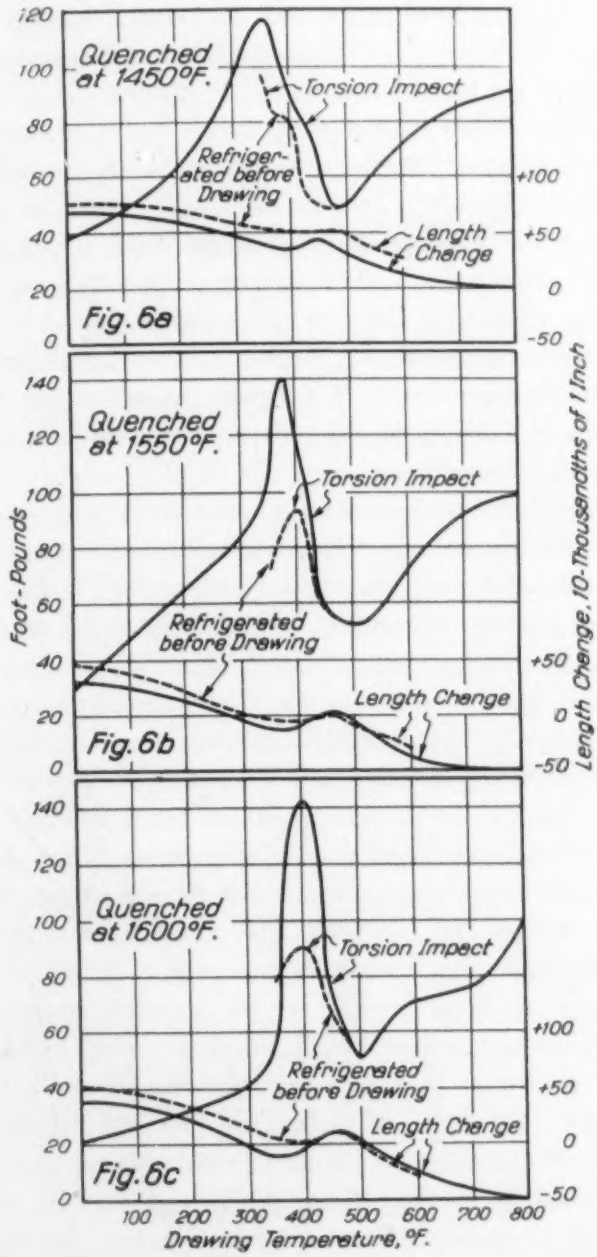


Fig. 6—Comparison of Torsion Impact and Length Change Curves on Brine-Quenched and Drawn Specimens, with Curves of Similar Specimens Quenched, Cooled in Liquid Air and Drawn. Tests made on 1.08 Per Cent Carbon Tool Steel Quenched at Three Temperatures and Drawn.

parison of the impact and volume change reveals an interesting fact, viz., that while the valley of the impact curve in every case occurs coincident with the end of the austenite transformation, the peaks

obtained on the series quenched at 1550 and 1600 degrees Fahr. (845-870 degrees Cent.) lag behind the start of austenite transformation, the degree of lag increasing with higher quenching temperatures. This is probably the result of more highly stressed martensite as the quenching temperature is increased, with consequent delayed recovery of ductility.

Fig. 5 shows that the drop in impact resistance is coincident with austenite breakdown. The questions which now arise are:—First, does the high peak of toughness result from the presence of austenite acting as a cushioning agent, and second, does the loss of austenite per se account for the drop in impact down to the valley, or is this drop the result of micro stresses caused by expansion as the austenite transforms?

It was felt that these questions could be definitely answered by cooling in liquid air several impact specimens previously quenched at the three temperatures, subsequently drawing in the temperature zone under discussion. If these showed a lowering at the peak, but no lowering at the valley, it would be reasonable to conclude that the drop in the curve is the result of loss of austenite per se, rather than the result of stress. Consequently a series of specimens quenched at each of the three temperatures was cooled in liquid air (—292 degrees Fahr.) and drawn at temperatures from 350 to 500 degrees Fahr. (175-260 degrees Cent.). With each of these was carried a series of volume change specimens. Results are shown in the curves in Fig. 6, in which are included for comparison the impact and volume change curves previously shown in Fig. 5.

Comparison of these curves shows a much smaller expansion through the austenite transformation range upon the liquid air treated specimens, accompanied by a marked lowering of the torsion impact peak. Since the first stage of tempering has been shown to be one of stress relief, the changes occurring in this range would affect the martensite formed by the liquid air immersion as well as that originally formed on the quench. Consequently it is reasonable to conclude that the high ductility accompanying the peak of the impact curve is due to the presence of austenite, and that the drop in ductility is the result of the transformation of this constituent to the less ductile constituent, martensite.

Summary

The three stages in the characteristic torsion impact curve for a

quenched and drawn high carbon steel shown in Fig. 1, have been shown to coincide with the three universally recognized structural stages traversed in the tempering operation. The first structural stage is characterized by stress relief in the martensite. Coincident with this change the torsion impact curve rises from 0 to A. The second structural stage involves the transformation of retained austenite to martensite, accompanied by a drop in the impact curve from A to B. This stage has been studied in some detail, and it has been shown that the drop in the impact curve is caused by a rapid loss in ductility, which in turn results from the breakdown of austenite to the less ductile martensite. During the third structural stage martensite gradually decomposes to the softer more ductile constituents, with an accompanying rise in the torsion impact curve from B to C.

It is thus seen that the torsion test reveals some very important fundamental properties of hardened and drawn tool steel. The very fact that these properties are fundamental however, makes it necessary to apply the test to practical problems with care, and with full knowledge of the design of the tool and its purposes. When such precautions are observed, the test becomes a valuable mechanism for the selection of proper heat treating procedure, and thus affords a means of control which should make for better and more uniformly heat treated tools.

The authors wish to gratefully acknowledge the help of Dr. A V. deForest in making the permeability tests recorded in Fig. 5.

Appendix

Referring to Fig. 7, in a cylindrical section the forces acting under torsion may be considered as concentrated on a circumference whose radius is the polar radius of gyration.

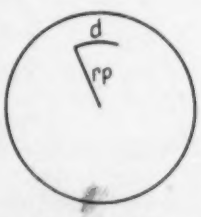


Fig. 7—Diagram Illustrating Forces Acting Under Torsion in Cylindrical Section.

In Fig. 7, r_p represents the polar radius of gyration

r is the radius of the specimen or 0.125 inch

$$\text{Since } r^2_p = \frac{r^2}{2}, \quad r_p = 0.707r = 0.0884 \text{ inch}$$

If d is distance in feet through which forces act,
α is the angle of twist in degrees
and S is shearing strength of the material in pounds per square inch then the work done in rupturing the piece, disregarding that portion of the work expended in distorting the specimen elastically may be expressed as:

$$(1) \qquad W_2 = \pi r^2 dS$$

$$\text{Since } d = \frac{2\pi r_p \alpha}{360} \text{ and } \pi r^2 = .049, \text{ the equation becomes}$$

$$(2) \qquad W_2 = \frac{\pi r_p \alpha S}{3670}$$

$$\text{Since } r_p = \frac{0.0884}{12} \text{ or } 0.00736 \text{ feet}$$

$$(3) \qquad W_2 = \frac{\alpha S}{158800}$$

Considering now the work of elastically deforming the specimen, the deflection formula for stresses under the elastic limit is

$$(4) \qquad \theta = \frac{pPl}{FJ}$$

in which θ = angle of torsion under EL
P = resultant of twisting force in pounds
p = distance from axis in inches
l = length of shaft in inches
F = torsional modulus 12,000,000
J = polar moment of inertia

$$= \frac{1}{32} \pi d^4$$

P in this case = .049S, in which S is assumed to be approximately the elastic limit
p = 0.0884 inch, the polar radius of gyration
l = 1

$$J = \frac{3.1416 \times 0.0039}{32} = 0.00039$$

from equation (4) consequently

$$\theta = \frac{0.049S \times 0.0884}{12000000 \times 0.00039} = 0.000000925S \text{ radians} \tag{5}$$

If d is the distance through which the forces act

$$d = \frac{0.000000925S \times 0.0884}{12} = 0.681 \times 10^{-8}S \text{ ft.} \tag{6}$$

The work expended in twisting up to elastic limit consequently is

$$W_1 = \frac{0.681 \times 10^{-8}S \times 0.049S}{2} \text{ or,}$$

$$W_1 = 0.167 \times 10^{-9}S^2 \tag{7}$$

Combining equation (3) and (7) the total work of rupture is

$$W = W_1 + W_2$$

$$\text{or } W = \frac{aS}{158800} + 0.169 \times 10^{-9}S^2$$

Simplifying, $W = 0.00000629aS + 0.169 \times 10^{-9}S^2$

$$W = S\,(0.629 \times 10^{-5}a + 0.169 \times 10^{-9}S)$$

Bibliography

1. Luerssen and Greene, "The Torsion Impact Test," *Proceedings*, American Society for Testing Materials, Vol. 33, 1933, p. 315.
2. Luerssen and Greene, "The Torsion Impact Properties of Tool Steel," TRANSACTIONS, American Society for Metals, Vol. 22, 1934, p. 311.
3. Howard Scott, "Dimensional Changes Accompanying the Phenomenon of Tempering and Aging Tool Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 9, 1926, p. 277.
4. Heindlhofer and Wright, "Density and X-ray Spectrum of Hardened Ball Steel Tempered at Various Temperatures," TRANSACTIONS, American Society for Steel Treating, Vol. 7, 1925, p. 34.
5. Georg Kurdyumov, "The Heat Treatment of Carbon Steels in the Light of X-ray Researches," *Archiv für Eisenhüttenwesen*, Vol. 6, Sept. 1932, p. 117-123.
6. A. V. deForest, "A New Method of Magnetic Inspection," *Proceedings*, American Society for Testing Materials, Vol. 23, 1923, p. 611.
7. Scott and Movius, "Thermal and Physical Changes Accompanying the Heating of Hardened Carbon Steels," Bureau of Standards Scientific Papers No. 396, 1920. TRANSACTIONS, American Society for Steel Treating, Vol. 1, 1921, p. 758.

8. E. Maurer, *Revue de Metallurgie*, Vol. 5, 1908, p. 711.
9. Guillet and Portevin, "Metallography and Macrography," McGraw Hill Co., 1922, p. 104.
10. O. V. Greene, "Some Characteristics of Pearlite in Eutectoid Rail Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 69.
11. J. V. Emmons, "Some Physical Properties of Hardened Tool Steel," *Proceedings*, American Society for Testing Materials, Part II, Vol. 31, 1931, p. 47.

DISCUSSION

Written Discussion: By R. Schempp, metallurgist, Halcomb Steel Co., Syracuse, N. Y.

The authors are to be congratulated on the excellent work as represented in their paper, dealing with torsional impact properties of carbon tool steels, and in the manner in which they have explained the toughness and brittleness phenomena, as determined by the torsional impact test.

Similar to these phenomena, the much discussed blue heat brittleness in steels, which causes a loss of ductility, elongation and reduction of area—and therefore reduced toughness characteristics—has been attributed to an aging, which is a precipitation process. This process can be looked upon as a function of distortion, time and temperature and may occur in any solvent lattice, the solubility of which decreases toward room temperature. The variables; that is, distortion, time and temperature, may either work together or in opposition to each other and may thereby result either in an intensification or diminution in the above process.

Drastically quenched steel is an aggregate of austenite and martensite, with the latter constituent predominating; austenite being an interstitial solid solution of carbon in gamma iron (face-centered cubic), while martensite is believed to be an interstitial solution of carbon in tetragonal or body-centered ferrite.

As austenite is a homogeneous solid solution, it is stable as long as it remains in situ; while on the other hand martensite, being of transitional solid solution characteristics, is not in a state of equilibrium and, with adequate distortion, time or temperature, will attempt to re-establish equilibrium conditions; namely, ferrite plus carbide.

Martensite may exist in two distinct forms or phases; that is, alpha or beta. Tetragonal or alpha martensite occurs on the surface of drastically quenched steels and is harder and more stable than the beta or body-centered martensite which is formed in towards the interior of the quenched specimen. (The former phase of martensite, in microscopical examination, may be distinguished from the latter due to its whiter appearance.)

Heating to approximately 150 degrees Cent. (300 degrees Fahr.) or slightly higher, will start precipitation, causing a conversion of the alpha martensite into the more stable beta form with a change in the axial ratio (c/a) of 1.07-1.03 to 1, and consequently, producing slip resistance, loss of ductility, elongation, reduction of area, torsional impact values, etc.

With progressing transformation, slip resistance diminishes rather quickly,

and at approximately 210 degrees Cent. (410 degrees Fahr.), the curve resumes its original direction.

Further increase in temperature, however, will affect the remaining austenite, creating unstability which is followed by transformation and precipitation to martensite, and, in turn, furthering slip resistance and intensifying the downward slope of the curves, as shown by the authors. This process will continue until transformation is complete. Further application of heat exceeding this temperature will then produce an agglomeration and coagulation of the precipitated particles and cause an increase in ductility and related physical properties.

Messrs. Luerssen and Greene's work has certainly connected the long neglected gap between the information and data known to the scientifically trained metallurgist by their explanation of this well known toughness or brittleness phenomenon, and the results which are encountered daily by the practical heat treater.

Written Discussion: By F. G. Tatnall, Baldwin-Southwark Corp., Philadelphia.

A new kind of test catches on slowly despite apparent value. Impact properties of hard and brittle materials had been a blind spot prior to the researches of Luerssen and Greene. Still such important tests as these grow slowly in general acceptance until there is found a means of tying them up with other physical properties more commonly known.

Perhaps this paper is only the beginning of correlation of torsion impact and other well known properties but even though the authors explore no further into physical relationships they, in this paper, seemed to have established torsion impact as no longer mysterious nor oddly detached.

In spite of the fact that Izod and Charpy tests could not be related by any stretch of the imagination to other physical properties, nevertheless these tests are generally accepted because impact is important and must be tested for.

References to torsion impact do not yet appear frequently and casually in technical literature but I venture to say that this test is building up such strength as will bring it into general acceptance despite all prejudice against adding more tests to a number which already seems so numerous as to be burdensome. Correlating various tests is consolidating the field of testing and bringing to it strength and prestige.

Unlike other impact tests which are designed to get one answer, torsion impact reaches out into several intriguing dark places and suggests a means of investigating the properties of plastics, ceramics, case hardened steels, chilled and white cast irons and of studying surface conditions of materials such as those containing submicroscopic pits due to corrosion or anything else affecting the surface where stress is a maximum in torsion. The effect of impact on members in torsion such as axles and shafts is further a matter of interest. The simplicity of the test recommends it for it is difficult to make a mistest.

Prior to the disclosure of the scheme for measuring torsional deformation in the test specimen as described in the Luerssen and Greene paper, torsion impact was said to be quantitative but not qualitative, so a static torsion test was recommended for qualitative study to see whether a high energy absorption value was due to high strength and lower ductility as in the martensitic struc-

ture or to higher ductility and lower strength as characteristics of the troostitic or sorbitic structures with lowest energy values in the series appearing in mixed structures of austenitic-martensitic, or martensitic-troostitic. Now we find evidence that the quick, utterly simple, torsion impact test becomes qualitative as well as quantitative which is important news for the metallurgical laboratory.

Written Discussion: By Howard Scott, Westinghouse Research Laboratories, East Pittsburgh, Pa.

The authors' interpretation of the torsion impact test is chiefly concerned with the significance of constitutional effects. This treatment of the subject is of course quite pertinent, but it ignores the distinctive challenge to the testing engineer that their original work has presented, namely, the pronounced failure of the test results to conform with those of tension or bending. Until we can explain this lack of conformity, our knowledge of metal failures is on a very insecure foundation. If our basic concepts were adequate, the results would have been obvious. There remains then the fundamental question: Why do the torsion impact curves not conform substantially with those of bending impact?

The new information presented in this paper and particularly that on angle of twist will undoubtedly be of material value in answering the foregoing question. This is the third of a series of papers that will undoubtedly be a dominant factor in leading to a more comprehensive knowledge of the mechanism of fracture of metals.

Written Discussion: By R. S. Rose, metallurgical department, Vanadium-Alloys Steel Co., Latrobe, Pa.

The present contribution of Messrs. Luerssen and Greene makes use of magnetic and length change measurements in accounting for the abrupt loss of impact strength upon tempering hardened carbon tool steel beyond about 390 degrees Fahr. In addition to correlating angular plasticity with the trend of the impact curve, they show the minimum impact value coincident with the completion of the austenitic transformation. There is an abundance of evidence available from the literature marking this at about 500 degrees Fahr. in carbon steels.

It would seem of some significance to make reference to investigations of very low alloy high carbon steels wherein similar results were obtained and identical explanations advanced. Bain and Grossmann[1] using a water and oil hardening high carbon low tungsten steel found a peak toughness at 400 degrees Fahr. followed by a valley at 500 degrees Fahr. coincident with the completion of the volume expansion. The same authors[2] using a high carbon medium manganese steel found a peak impact at about 450 degrees Fahr. and a minimum at 550 degrees Fahr. again coinciding with the completion of the volume expansion. The small alloy content of these steels appears not to have appreciably altered the temperature of structural change characteristic of straight carbon steel. Using an X-ray method, which is undeniably of greater

[1]M. A. Grossmann and E. C. Bain, "On the Nature of Some Low Tungsten Tool Steels," TRANSACTIONS, American Society for Steel Treating, 1926, Vol. 9, No. 2, p. 259.

[2]E. C. Bain and M. A. Grossmann, "The Nature of Oil Hardening Non-Deforming Tool Steels," TRANSACTIONS, American Society for Steel Treating, 1926, Vol. 10, No. 6, p. 883.

reliability than the magnetic method used by Messrs. Luerssen and Greene, they showed complete disappearance of the characteristic austenitic lines at 500 degrees Fahr. corresponding to the maximum increase in length and approximately with the minimum impact value. G. A. Ellinger[3] in reporting results of a thermomagnetic analysis of steel showed rather conclusively that the increase in magnetization upon tempering quenched carbon steel up to about 390 degrees Fahr. was due mainly to release of stress and not austenitic decomposition. Apparently this is due to the disappearance of the tetragonal lattice.

It thus seems quite well established that a drop in toughness occurs in carbon and low alloy steels in the temperature range of austenitic decomposition. It does not follow that this can be accepted as proof that the loss of toughness is entirely the result of the loss of retained austenite. The available evidence strongly suggests that carbide formation resulting both from austenitic decomposition and precipitation from the supersaturated ferrite to be mainly responsible for the abrupt loss of toughness. This might be construed as a different expression of the same interpretation as that of the authors. However, the emphasis is placed upon the brittleness imparted by the carbide formation possibly of some critical size, and not upon the toughness induced by retained austenite. Thus carbide formation results in the falling of the impact curve and does not require retained austenite although presence of this latter phase increases the magnitude since additional carbide is formed at the specific temperature involved. Honda[4] and Öhman[5] admit the likelihood of ferrite supersaturation after the disappearance of the tetragonal lattice. It is a well known fact that the precipitation or formation of a compound is generally accompanied by a decrease in impact value, and Houdremont[6] has definitely shown this to be the case in tempering high carbon vanadium steels. The impact curve in tempering stainless iron shows a tremendous drop upon tempering at about 1000 degrees Fahr. and must be attributed to a precipitation phenomenon since very little austenite can be retained. There is some evidence to indicate that the first appearance of carbide in tempering a quenched 0.75 per cent carbon steel is 455 degrees Fahr. Since no measurements were made between 390 and 455 degrees Fahr. it seems very probable that a small amount is formed between these two temperatures. No carbide could be detected below 390 degrees Fahr. Carbide formation therefore occurred between the temperatures of 390 and 570 degrees Fahr., being complete at the latter temperature. These results are based upon determination of A_o, the sensitivity of which may be open to question. These temperature ranges coincide remarkably well with the peak and valley of the

---

[3]Raymond L. Sanford and George A. Ellinger, "Thermomagnetic Phenomena in Steel and their Application in the Study of Tempering of Quenched 0.75 Per Cent Carbon Steel," TRANSACTIONS, American Society for Steel Treating, 1932, Vol. 20, No. 3, p. 263.

[4]Kotaro Honda and Zenji Nishiyama, "On the Nature of the Tetragonal and Cubic Martensites," TRANSACTIONS, American Society for Steel Treating, 1932, Vol. 20, No. 5, p. 464.

[5]Einar Öhman, "Endurance of Steel Depends on Structure, Strength and Ductility," *Metal Progress*, 1931, Sept., p. 88.

[6]E. Houdremont, H. Bennek and H. Schrader, "Hardening Power and Tempering of Steels Containing Carbides of Low Solubility, Especially Vanadium Steels," *Metals Technology*, 1934, December, Technical Publication No. 585.

impact curve of a 0.90 per cent carbon steel previously reported by the authors.

If as suggested in this discussion, carbide formation occurring during the tempering of quenched carbon tool steel from both austenitic decomposition and supersaturated ferrite is responsible for the loss of toughness, then we might expect two peaks and two valleys in an impact curve of alloy tool steel wherein austenitic decomposition and precipitation from supersaturated ferrite do not occur simultaneously.

Written Discussion: By S. C. Spalding, metallurgist, American Brass Co., Waterbury, Conn.

We have studied with considerable interest this latest paper from the Carpenter Steel Co.'s metallurgists. The earlier papers dealt more with the presentation of the data, while this one deals more with causes. We have never questioned the data presented or the conclusions that this data represented in a very graphical way some changing properties of the test pieces. We did question, however, as brought out in previous discussion, the propriety of saying that the points of maximum toughness as shown by the torsion impact tests represented real points of maximum toughness of tools in practice, or, in other words, how far the results could be utilized to guide us in the heat treatment of tools. Apparently, in the light of the further work which they have now done, the authors too are somewhat in doubt as borne out by their statement near the close of the paper, as follows:

"It is thus seen that the torsion test reveals some very important fundamental properties of hardened and drawn tool steel. The very fact that these properties are fundamental, however, makes it necessary to apply the test to practical problems with care and with full knowledge of the design of the tool and its purpose."

We have studied the paper carefully and the reasoning as presented. Following these lines, we observe that:

On tempering to 350 degrees Fahr. the only result is strain relief, no structural change, rise in torsion impact toughness found, therefore—due to strain relief. From 350 to 450 degrees Fahr. martensite is being precipitated from the retained austenite, hence, drop in ductility and torsion impact toughness. From 450 degrees Fahr. on up, tempering of martensite to troostite and sorbite is occurring with increased ductility, hence, rise in torsion impact figures. This is our interpretation of the authors' explanation of the phenomena.

Now, let us consider the data in reference to hardness instead of torsion impact toughness and see how the same theories apply. The Rockwell hardness values, as shown by the authors, fall more or less steadily over the entire range. We then say that up to 350 degrees Fahr. we are getting only strain relief and the falling in hardness is due to relief of strains. From 350 to 450 degrees Fahr. we are precipitating martensite and the still falling hardness is due to the formation of martensite, even though martensite is the hardest structural condition of tool steel, then, from 450 degrees Fahr. on we are tempering this martensite and the hardness still drops. The apparent contradiction in the range, 350 to 450 degrees Fahr. might be explained by saying that the precipitation of martensite was only taking place in the

retained austenite, which was a small proportion of the whole, and that at the same time the martensite formed at quenching was being tempered and this effect predominated, resulting in lower hardness values, yet, if this were the case, why should ductility decrease?

If the tempering of the quenched martensite overshadows the precipitation of retained austenite, as is indicated by the drop in hardness, why does not the increasing ductility from this cause also predominate? We feel that regardless of the torsion impact findings, in actual cases it does and that as the draw is increased, hardness falls and ductility increases.

To support this statement, we can cite several cases. First—let us consider the humble grinding crack in tool steel. I believe we will all admit the cause is due to lack of plasticity in the hardened surface to accommodate itself to the rapid expansions set up by local wheel heating. This being true, any treatment of a hardened surface which increases its plasticity should decrease the susceptibility to cracking from this cause. Turning now to some observations by Brophy in a paper on "Grinding Cracks," Vol. 18 of TRANSACTIONS, he shows illustrations of samples of 1.16 per cent carbon tool steel hardened at various temperatures and tested for grinding cracks; at no draw, at 300 degrees Fahr. draw and 480 degrees Fahr. draw. For details I refer you to his paper but the gist of it is at no draw he gets plenty of cracks, at 300 degrees Fahr. draw some cracks, and at 480 degrees Fahr. draw no cracks, although the 480 degrees Fahr. draw is in the torsion impact most brittle nonplastic range; also—in another test tempered at 390 degrees Fahr. some cracks were found, although not as many as when untempered, yet, at 390 degrees Fahr. the hard surface, according to the torsion impact diagnosis, should be at about maximum plasticity.

Next, we will take a spring made of a 1.00 per cent carbon steel, as many were before the advent of alloy steels. According to the torsion impact figures, this spring would be tougher if drawn at 350 degrees Fahr. than at 650 to 800 degrees Fahr. The value in one case being 125 foot-pounds at 350 degrees Fahr. and only 90 foot-pounds at 800 degrees Fahr. and 80 foot-pounds at 650 degrees Fahr. Experience, however, denies this as we know that springs drawn at 350 degrees Fahr. would be brittle and break, while thousands of successful springs are drawn at the 650 to 800 degrees Fahr. range.

One further point which might be noted is that most tools have appreciable mass and the hardened layer to which, supposedly, the torsion impact properties apply is only a superficial one. The balance of the tool is made up of a moderately soft core which, admittedly, would not follow the curve. The properties of the finished tool, naturally, are the results of the effect of hardening and drawing on the composite mass, which makes it questionable whether a treatment designed from a torsion impact test, with only one constituent in mind, would be most suitable.

Oral Discussion

A. V. deFOREST:[1] It seems to me that this paper, like the one before it, is opening a way of investigating some of the very intricate features in

[1]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

mechanical testing, particularly in regard to rapid rates of deformation, of which we know perhaps less than nothing at the present time.

We have at present the utmost confusion in the interpretation of notch bar impact values in engineering structures. If the bar is weaker in notch impact and stronger in the un-notched impact, is it or is it not a better piece of steel than its corresponding rival? We just do not know. This torsion test, it seems to me, brings out one point in metallurgical structure which is not indicated by many other tests, and that is the immense importance of the retained austenite. If we look at it on a large scale we see a hard martensitic structure which is enclosed in a thin mesh of a rather ductile, somewhat unstable glue of austenite, and that glue has the property of hardening rapidly under further deformation, so that the austenite when it is deformed by cold work hardens very much more rapidly than ferrite. It seems reasonable that the torsional impact reaches its high values because of the self-hardening property of the austenite under deformation.

Authors' Closure

We greatly appreciate Mr. Schempp's discussion. In general his interpretation of the various parts of the impact curve agree closely with ours. We should like to point out, however, that he refers in one part of his discussion to alpha martensite as being the more stable form, and then later refers to it as being less stable than the beta form. The alpha or tetragonal form is usually assumed to be the unstable form, changing to the cubic at low ranges of drawing temperature.

Mr. Spalding's discussion shows a very close study of the paper. His comment with regard to the drop in Rockwell hardness coincident with the drop in impact is much in order, and we have given a great deal of thought to this apparent anomaly. It was in order to throw more light upon this point that we attempted to secure as nearly as possible an entirely martensitic structure after a 350 degrees Fahr. draw by treating in liquid air after the quench. Our results indicate quite clearly that the impact peak dropped as a result of austenite transformation accomplished without exceeding a drawing temperature of 350 degrees Fahr. It seems quite reasonable therefore that the amount of austenite transformed between 350 and 450 degrees Fahr. after the usual quenching procedure would be sufficient to account for the loss in impact resistance through this range. We believe that Mr. Spalding's interpretation of the structural changes occurring in this drawing range is perfectly in order, and that we have occurring both transformation of austenite and a slight breakdown of martensite already there, with attendant drop in hardness.

Mr. Spalding's comments with regard to grinding checks are very interesting, but we wonder if a drawing temperature of 300 degrees Fahr. is quite high enough to insure against the occurrence of checks in grinding. It has been our experience that under certain conditions it is too low and that it is necessary to draw thoroughly at 350 or 375 degrees Fahr., after which treatment the danger of grinding checks is practically eliminated.

With regard to the direct application of the test to practical tool problems, we have always attempted to point out the limitations of the test on such applications. We selected an arbitrary 1-inch test length for the pur-

pose of distributing stresses, and testing a fundamental property which probably could not be determined in the notched bar type of test. We selected a ¼-inch diameter section so that the test length would harden through uniformly in all types of steel, recognizing that if two different structures were present in the test bar this variable would lead to complications. The test consequently shows the properties of the structure occurring on the surface of the tool, which we believe should constitute a sound procedure since the maximum stresses usually occur on the surface in practice. Future work on composite structures, that is upon sections containing a soft core, is in prospect, but a great deal of work will be required to correlate such work.

Mr. Spalding's reference to the advantage of drawing springs at a high temperature is interesting, but we wonder whether the determining factor in spring quality is really impact resistance, or whether it is not rather fatigue resistance. In any event it will be well to point out some observations we have made in the course of our test work which may throw some light on this subject. We find a distinct difference in the character of the permanent twist within the drawing range of 350 to 450 degrees Fahr., and the drawing ranges above 450 degrees Fahr. In the lower range, in which some retained austenite is still present, the helix or twist is quite uniform from one end of the test length to the other. In the specimens drawn above 450 degrees Fahr. on the other hand, the twist tends to localize itself at some point on the test length. It is interesting to note the analogy between these torsion specimens and tensile specimens of austenitic and nonaustenitic steels. The austenitic tensile piece tends to elongate uniformly over its test length, while the nonaustenitic steels tend to elongate locally resulting in the familiar phenomenon of necking down just before rupture.

These observations bring out another important point, namely that the relative torsion impact values in these two ranges of drawing temperature will depend upon the test length. If test lengths were considerably shortened, say to ¼ inch, the tendency would be to greatly increase the ductility results on specimens drawn over 450 degrees Fahr., which would result in a relatively higher impact value. These observations open an interesting field of investigation into the effect of restricted test lengths and notches, which probably will throw a great deal of light on this entire subject.

Mr. Scott's discussion suggests several new angles for future work.

Mr. Rose suggests the interesting possibility that critical carbide size might account in part for the impact valley. In the carbon steels there is of course no positive evidence to support this theory, while we have on the other hand very positive evidence of the influence of austenite transformation. Nevertheless Mr. Rose's comments upon the possibility of two peaks on certain alloy steels in which austenite transformation occurs at a considerably higher temperature, are interesting. In fact this is more than simply a possibility, since a valley actually does occur in the high carbon high chrome and high speed steels, dividing two peaks of toughness. It is quite possible that this valley can be accounted for by coalescence of carbides as suggested by Mr. Rose. The valley, however, is minor as compared to the valley resulting upon the breakdown of retained austenite at the higher temperatures.

We thank Dr. deForest and Mr. Tatnall for their constructive remarks.

CONTRIBUTORY EFFECTS OF FURNACE ATMOSPHERES ON THE GRAIN-SIZE OF MOLYBDENUM HIGH SPEED STEEL

By Arthur Phillips and M. J. Weldon

Abstract

A study has been made of the effects of several furnace atmospheres on the grain-size, temperature of incipient melting and extent of decarburization of a molybdenum high speed steel (Mo 7.05; Cr 3.93; Va 2.03; C 0.77 per cent). The heat treatments from the standpoints of temperature and time covered a wide range, although particular attention was devoted to the experimental conditions closely approaching standard hardening practice. It was found that the most pronounced structural alterations are produced by oxidizing atmospheres, particularly those containing an appreciable water vapor concentration. No evidence was obtained that the grain growth and other abnormal effects of oxidizing atmospheres are due to "self-heating" of the steel as suggested by Gill in referring to Tour's results on tungsten high speed steel.

MOLYBDENUM has been regarded for many years as the most promising substitute for tungsten in high speed steel. It is believed that Mushet, prior to 1880, used this element in some of his self-hardening steels. In 1904 Guillet (1)[1] suggested that the hardening effect produced by a given concentration of tungsten may be obtained by only one-fourth as much molybdenum. Taylor, (2), in referring to the Taylor and White patent, stated that one per cent of molybdenum is equivalent to about two per cent of tungsten in steels of the high speed type. The 1:2 ratio seems to be rather definitely established in the molybdenum high speed steels of today, although the full equivalency of 18 per cent tungsten is often attained by the addition of another element which supplements the effect of the chief alloying element molybdenum. It is interesting to note that the substitutional ratio is the ratio of the atomic weights

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. Of the authors, Arthur Phillips is Professor of Metallurgy, and M. J. Weldon is a Graduate Student, Department of Metallurgy, Yale University, New Haven, Conn. Manuscript received June 1, 1935.

of these two metals, namely, molybdenum 96 and tungsten 184.

Until recently, progress in the development of molybdenum high speed steels has been rather generally restricted to sporadic experimental activity stimulated at times by threats of a tungsten shortage. Many of the earlier investigators were discouraged by certain difficulties encountered in the processing of the steels, particularly in the alloys containing more than about 5 per cent molybdenum. Today experienced alloy steel makers report no serious problems with regard to the melting and working of the commonly used analyses. One characteristic of high molybdenum steels noted early in their development is the pronounced tendency to decarburize and demolybdenumize[2] at the high temperatures required for proper heat treatment. Although the loss of these elements has been found to be greatly reduced by the use of a coating of borax or by heating in a selective furnace atmosphere, this troublesome practical consideration has had without doubt a marked retarding influence in the industrial acceptance of the steel.

During the last five years molybdenum high speed steels have been more favorably regarded both by the makers and users of tool steels. In the opinion of many experienced steel men, tools made of modern molybdenum high speed steel may be considered as the equivalent in performance of 18 per cent tungsten steel. In view, however, of the conflicting reports regarding the relative merits of the two steels, and considering the limited industrial history of the newer alloy, this conclusion in its broadest interpretation must be regarded as somewhat premature and subject to the test of time. It can be said, however, that certain types of molybdenum high speed tools have equalled, and in a few cases surpassed, the performance of the standard tungsten steel. The recent impetus to the serious consideration of the new steels may be attributed in large part to the comprehensive research program carried on for a number of years at the Watertown Arsenal (3) and more recently to the studies of J. V. Emmons (4).

Grain Growth Characteristics of Seven Per Cent Molybdenum Steel

The first part of the present experimental program was devoted

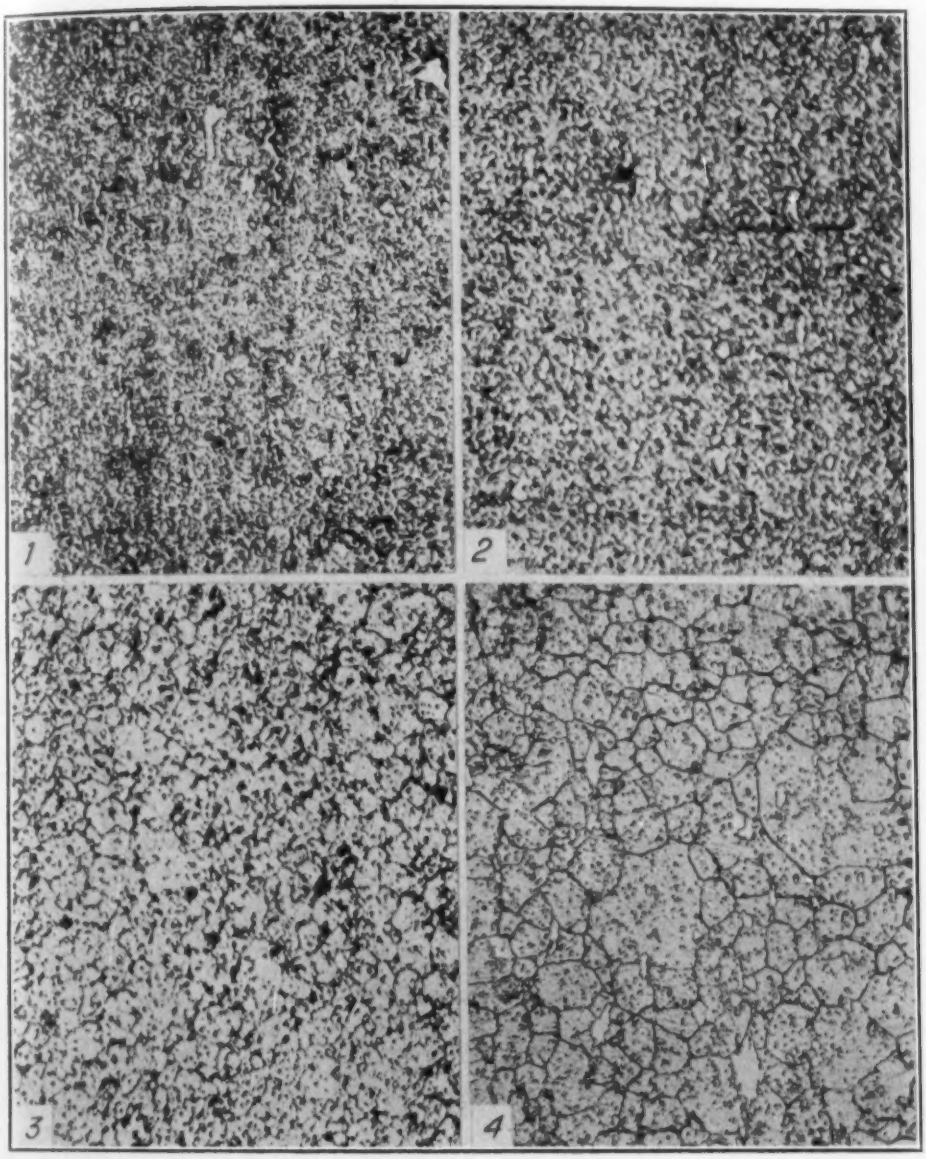
[2]It has been reported by several workers that although some molybdenum is lost by the volatilization of MoO_3, the soft skin may be attributed essentially to a substantial loss of carbon. In this work the term "decarburization" will be used to include all surface changes in composition.

to the investigation of a molybdenum high speed steel heat treated within a broad temperature range in atmospheres representing extreme oxidizing and reducing conditions as well as in atmospheres normally maintained in good industrial practice. The material used was hot-rolled and annealed sheet (0.065 inch thick, Rockwell hardness C-scale 29) having the following analysis:

	Per Cent
Carbon	0.77
Manganese	0.32
Silicon	0.47
Chromium	3.93
Molybdenum	7.05
Vanadium	2.05
Tungsten	0.07

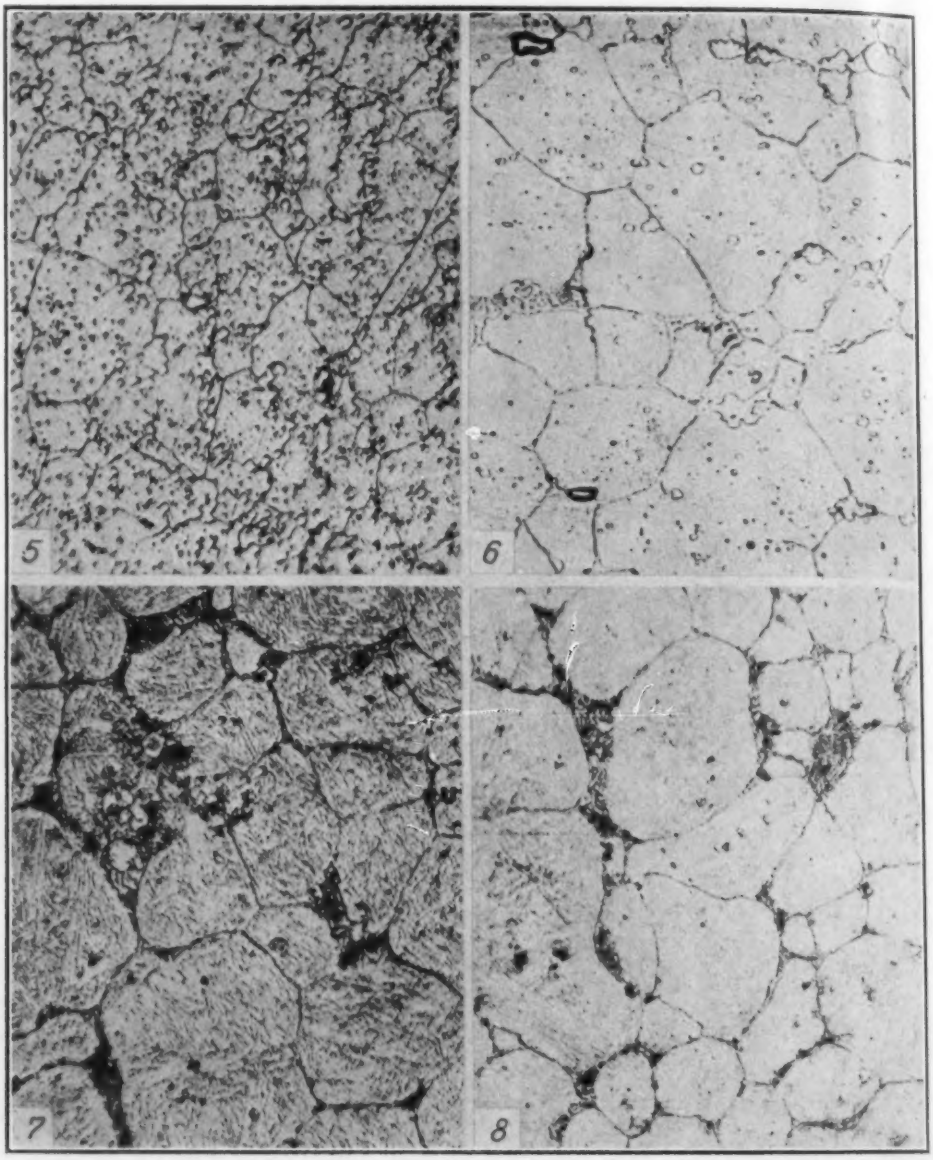
The specimens were prepared in the form of 1 x 14 inch strips numbered to designate their relative positions in the original sheet. All of the heat treatments were performed in the well known type of gas furnace containing a vertical carborundum muffle. Three holes in the base of the muffle permitted ready passage of the products of combustion upward through the muffle. Two units were employed, one for preheating and the other for the high temperature treatment. A tank containing a supersaturated aqueous solution of borax was located adjacent to the preheating furnace and an oil quenching bath, maintained at approximately 250 degrees Fahr. (120 degrees Cent.), was placed next to the hardening unit. In general, the hardening procedure was comparable to that followed in the conventional heat treatment of ordinary high speed in that the specimens were preheated for a definite time at 1500 degrees Fahr. (815 degrees Cent.) and then transferred to the hardening furnace. The total time in the latter furnace was 130 seconds and every precaution was taken to insure strict adherence to this time limit. Prior to the preheating, the strips were brought uniformly to a low red heat and then immersed in the borax bath. After removal from the solution, the residual heat in the specimen evaporated the water leaving a solid crust of borax which fused during the preheating to form a dense protective covering for the subsequent high temperature treatment. The use of borax is an expedient commonly utilized to protect this steel from decarburization.

In the first series of experiments a reducing atmosphere was maintained in both the preheating and hardening furnaces. The furnaces were operated by a man experienced in the heat treatment of



Photomicrographs of 7 Per Cent Molybdenum High Speed Steel. Specimens Etched in 5 Per Cent Nital. × 500.
Fig. 1—Quenched from 2095 Degrees Fahr. (1145 Degrees Cent.).
Fig. 2—Quenched from 2160 Degrees Fahr. (1180 Degrees Cent.).
Fig. 3—Quenched from 2210 Degrees Fahr. (1210 Degrees Cent.).
Fig. 4—Quenched from 2255 Degrees Fahr. (1235 Degrees Cent.).

this steel and he was directed to follow standard practice with regard to atmospheric conditions. After hardening, a cross section of a piece taken from the central part of each strip was examined microscopically with particular regard to grain-size, carbide distribution and degree of decarburization. The essential structural character-



Photomicrographs of 7 Per Cent Molybdenum High Speed Steel. Specimens Etched in 5 Per Cent Nital. × 500.
Fig. 5—Quenched from 2300 Degrees Fahr. (1260 Degrees Cent.).
Fig. 6—Quenched from 2345 Degrees Fahr. (1285 Degrees Cent.).
Fig. 7—Quenched from 2390 Degrees Fahr. (1310 Degrees Cent.).
Fig. 8—Quenched from 2440 Degrees Fahr. (1335 Degrees Cent.).

istics of specimens heated from 2100 to 2450 degrees Fahr. (1150 to 1345 degrees Cent.) are shown by Figs. 1 to 8. Although no evidence of decarburization was noted after hardening, the hardness values reported were obtained on ground surfaces. A study of the microstructures indicates that, under the specific conditions of these

Table I

Hardness Values (Rockwell C-Scale of Seven Per Cent Molybdenum High Speed Steel

	Quenching Temperatures					
	2160 Degrees Fahr. (1180 Degrees Cent.)		2210 Degrees Fahr. (1210 Degrees Cent.)		2260 Degrees Fahr. (1235 Degrees Cent.)	
Time (Sec.)	As Quenched	Drawn at 1050 Degrees Fahr. (565 Degrees Cent.)	As Quenched	Drawn at 1050 Degrees Fahr. (565 Degrees Cent.)	As Quenched	Drawn at 1050 Degrees Fahr. (565 Degrees Cent.)
30	61.0	59.0	62.5	61.0	62.4	61.0
60	63.3	61.5	65.0	64.0	64.5	65.5
90	64.9	63.0	65.1	65.0	63.7	65.5
120	64.6	62.0	64.7	66.5	63.2	65.0
150	64.9	65.6	65.2	66.0	63.4	66.5
180	63.5	65.5	64.4	66.0	63.6	66.0

heat treatments, the austenite grains become sharply defined after heating to about 2250 degrees Fahr. (1230 degrees Cent.). Grain growth, with progressive absorption of carbides, continues with increasing temperature until a temperature of about 2345 degrees Fahr. (1285 degrees Cent.) is reached. At this temperature incipient melting takes place, usually at the grain boundaries and around

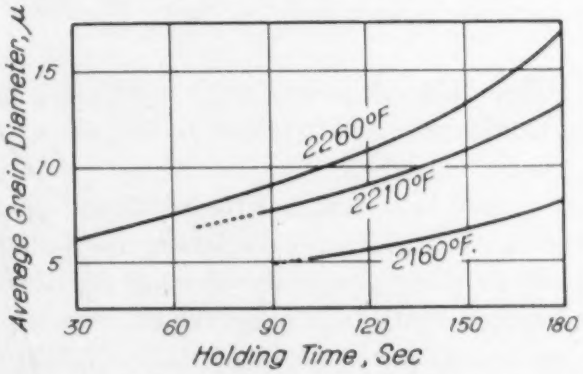


Fig. 9—Graphs Showing Grain Sizes Corresponding to Varying Periods and Temperatures.

the few remaining carbide particles. The coarser grained specimens reveal, especially after prolonged etching, the acicular markings which Grossmann and Bain (5) attribute to the presence of martensite.

The determination of the most favorable combination of the temperature and time variables for the proper hardening of this steel are of course outside the scope of this paper. In general, specific information of this kind must inevitably be obtained through industrial experience based largely on performance tests. However, some idea of the hardness values obtained by varying these two conditions within certain definite limits may be gained from Table I. This

table also includes the hardness tests made on specimens subsequently drawn for two hours at 1050 degrees Fahr. (565 degrees Cent.).

Grain sizes corresponding to varying periods at 2160, 2210 and 2260 degrees Fahr. (1180, 1210 and 1235 degrees Cent.) are plotted in Fig. 9. It is quite obvious from an inspection of the curves that time at temperature (within the limits set by industrial practice) is relatively unimportant at the lower temperatures but is a significant factor at the higher temperatures. For example, three minutes at

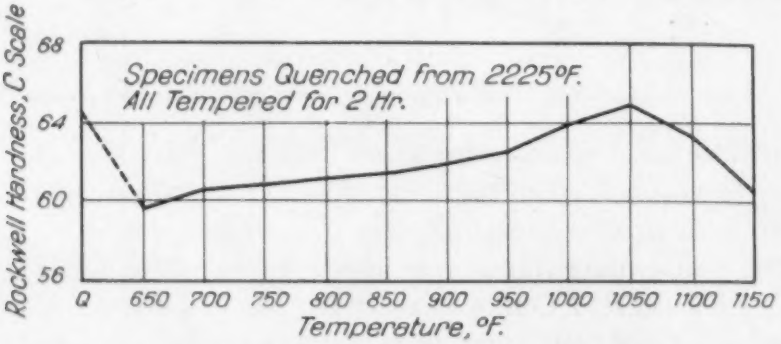


Fig. 10—Graph Showing the Effect of Drawing Temperatures on Material Previously Quenched from 2225 Degrees Fahr. (1220 Degrees Cent.).

2260 degrees Fahr. (1235 degrees Cent.) produces a grain diameter approximately three times that attained by 30 seconds at the same temperature.

In general, it may be stated that the structural changes involved in the drawing treatment (2 hours at 1050 degrees Fahr.) were found to be comparable to those ordinarily obtained by similar treatment on 18 per cent tungsten steel. The effect of drawing temperatures on material previously quenched from 2225 degrees Fahr. (1220 degrees Cent.) is shown by Fig. 10, which indicates that the maximum hardness is reached by treating at about 1050 degrees Fahr. (565 degrees Cent.). This curve was found to be indicative of the hardness changes produced by drawing this steel after quenching from a temperature sufficiently high to accomplish considerable solution of the carbides, without simultaneously developing excessively coarse grains. Specimens hardened at higher temperatures attained a somewhat higher hardness value; material quenched from below about 2200 degrees Fahr. (1205 degrees Cent.) showed no well defined hardness maximum.

During the preliminary experimental work, evidence was accumulated which suggested that the molybdenum high speed steels

are highly reactive with certain furnace atmospheres, particularly with regard to grain-size effects and surface concentration changes. The early work indicated that in order to obtain consistent results in determining the significance of the temperature and time factors on grain-size, a reasonably close control of furnace gas conditions was absolutely essential, even though borax was used as a protective coating.

As the first step in studying the effect of atmosphere on grain growth additional specimens, free of borax, were heated in reducing and oxidizing gases but under otherwise comparable conditions. By manipulation of the air supply, furnace atmospheres were obtained which may be designated as (a) "highly" reducing, (b) "slightly" reducing, (c) "slightly" oxidizing and (d) "highly" oxidizing. All specimens were first preheated to 1500 degrees Fahr. (815 degrees Cent.) in a slightly reducing atmosphere which was not varied during the treatments. The hardening temperature was maintained at 2225 degrees Fahr. (1220 degrees Cent.), irrespective of the nature of the atmosphere, and the specimens were held at temperature for 130 seconds. The results of the grain-size measurements are assembled in Table II. Surface changes are reported as simply the depth of visible decarburization expressed in terms of percentage of the total cross sectional area. Typical microstructures are shown by Figs. 11 to 14. An interesting contrast in grain sizes is noted in Figs. 15 and 16; the two specimens were given two heat treatments (i.e., at 2225 degrees Fahr.) as previously described, the former under "highly" reducing conditions and the latter under "highly" oxidizing conditions.

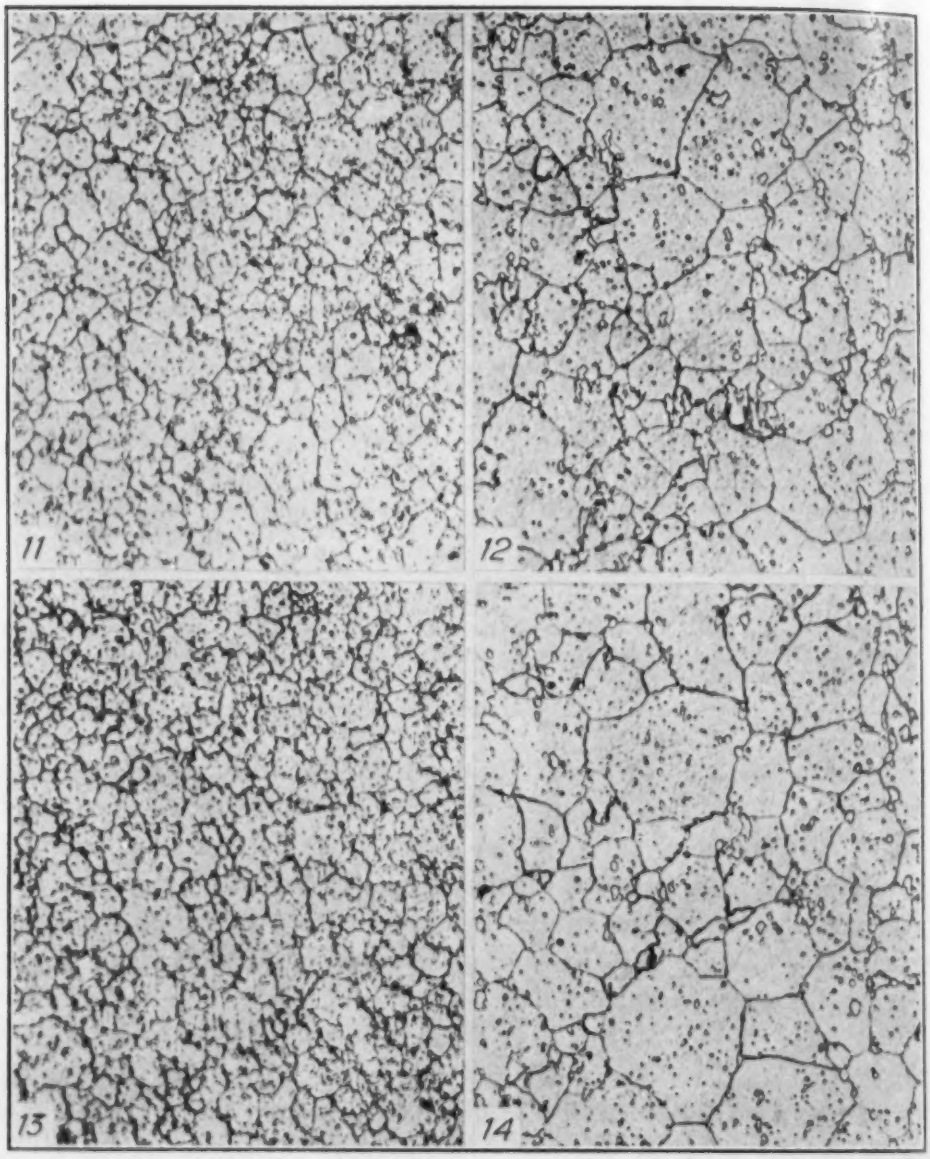
Table II

Effect of Furnace Atmospheres on Material Heat Treated at 2225 Degrees Fahr. (1220 Degrees Cent.)

Furnace Atmosphere	Average Grain Diameter in Microns	Rockwell Hardness ("C" Scale)	Percentage of Decarburization*
Highly Reducing	7	63.5	1.5
Moderately Reducing	9	64.3	6.9
Moderately Oxidizing	15	63.7	11.0
Highly Oxidizing	20	63.2	11.8

*Depth of decarburization at both surfaces expressed in terms of percentage of the total cross-sectional area.

In order to ascertain more definitely the protective value of a borax coating, a number of specimens so treated were heated simul-



Photomicrographs of 7 Per Cent Molybdenum High Speed Steel. Specimens Etched in 5 Per Cent Nital. × 500.

Fig. 11—Quenched from 2225 Degrees Fahr. (1220 Degrees Cent.) in a Slightly Reducing Atmosphere.

Fig. 12—Quenched from 2225 Degrees Fahr. (1220 Degrees Cent.) in a Slightly Oxidizing Atmosphere.

Fig. 13—Quenched from 2225 Degrees Fahr. (1220 Degrees Cent.) in a Highly Reducing Atmosphere.

Fig. 14—Quenched from 2225 Degrees Fahr. (1220 Degrees Cent.) in a Highly Oxidizing Atmosphere.

taneously with uncoated material. A study of Table III indicates that the same relative grain-size differences were produced by the two types of furnace atmospheres and the difference seems to be

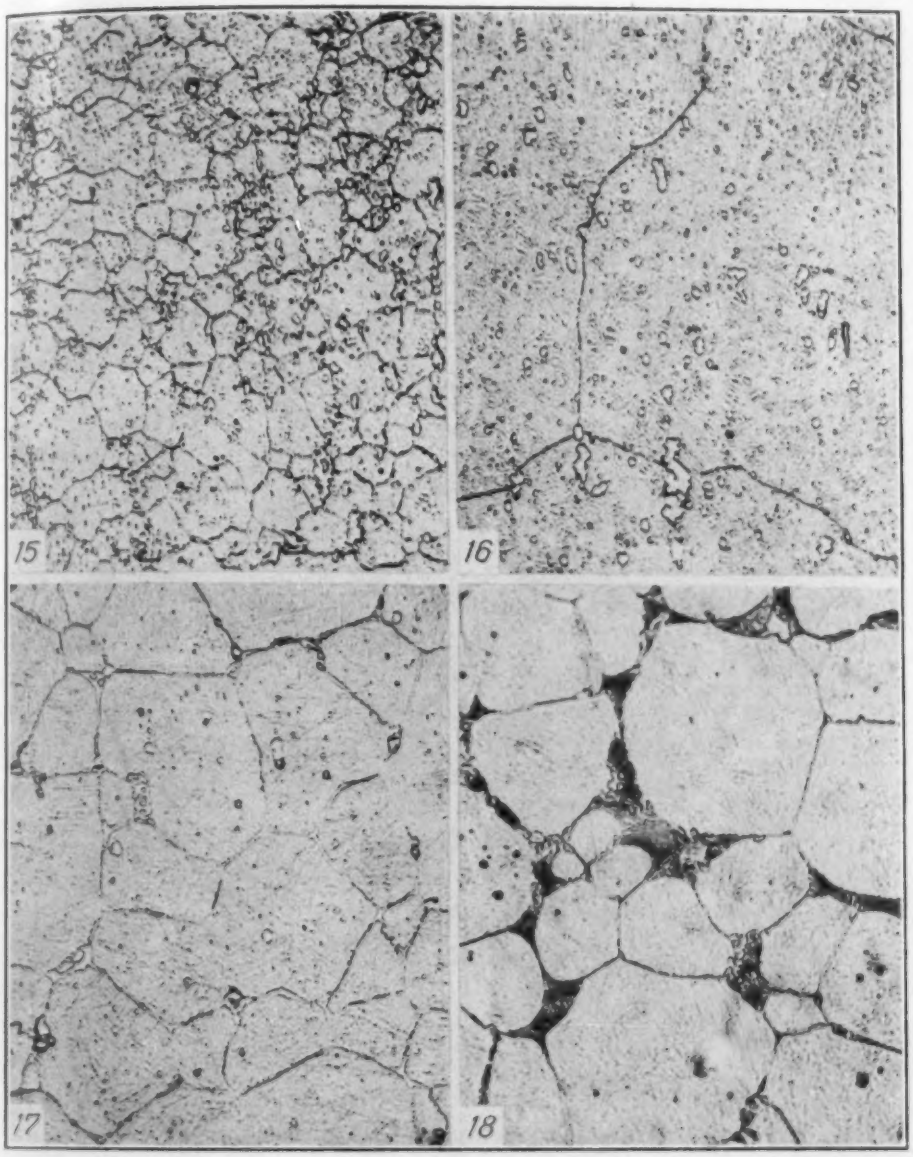


Fig. 15—Photomicrograph of 7 Per Cent Molybdenum High Speed Steel Heated to 2225 Degrees Fahr. (1220 Degrees Cent.), Quenched and Reheated to Same Temperature in a Highly Reducing Atmosphere. Etched in 5 Per Cent Nital. × 500.

Fig. 16—Specimen Heated in a Manner Similar to Fig. 15 in a Highly Oxidizing Atmosphere. Etched in 5 Per Cent Nital. × 500.

Fig. 17—Photomicrographs of 7 Per Cent Molybdenum High Speed Steel Quenched from 2335 Degrees Fahr. (1280 Degrees Cent.) in a Highly Reducing Atmosphere. Specimen Protected with Borax.

Fig. 18—Same as Fig. 17 Except that Specimen was Heated in a Highly Oxidizing Atmosphere while Protected with Borax. Etched in 5 Per Cent Nital. × 500.

reduced to no appreciable extent by the borax coating. Comparing the effect of the oxidizing atmosphere on the borax-coated and borax-free specimens, it is evident that, for the same temperature,

Table III

Average Grain Diameters (in Microns) and Per Cent of Surface Decarburization at Various Temperatures Under Reducing and Oxidizing Conditions

Temperature Degrees Fahr.	Reducing Atmosphere				Oxidizing Atmosphere			
	Borax Treated		Not Treated		Borax Treated		Not Treated	
	Grain Size	Decarburization	Grain Size	Decarburization	Grain Size	Decarburization	Grain Size	Decarburization
2150	5.0	none	...	none	5.5	none	5.8	2.0
2200	5.5	none	5.0	none	8.3	none	10.0	2.5
2250	8.3	none	8.5	6	14.0	none	12.5	8.0
2300	25.0	none	25.0	6	33.0†	none	30.0†	8.0
2335	27.0*	11	26.0*	12	30.0†	15	30.0†	15.0

*Showed incipient melting.
†Marked melting observed.

grain sizes of the same order were obtained, even though the borax-free material showed marked decarburization and the borax-coated specimens were substantially free of such surface changes. In other words, although borax apparently functions in protecting the surface from oxidation it has little influence on the grain-size of the subsurface metal. Another effect of highly oxidizing atmospheres within the temperature range investigated is evidenced by a comparison of Figs. 17 and 18. The latter structure shows unmistakable indications of fusion at the grain boundaries. The grain-size at the temperature of incipient fusion is substantially the maximum size produced under a given set of conditions as the fused metal at the boundaries serves rather effectively as a barrier to further growth.

Experiments with Special Atmospheres

At the conclusion of the treatments made in atmospheres which were essentially modifications of industrial furnace conditions it was decided to extend the investigation to include gas conditions not ordinarily associated with commercial hardening. Argon, a non-reactive gas, was chosen for the purpose of establishing a basic relationship between temperature and grain-size effects which might be considered to be free of atmospheric influence. The other gases chosen were air and carbon monoxide, the latter prepared by the decomposition of formic acid. Water vapor, in all cases, was removed by passing the gases through drying towers before their entry into the furnace. In order to remove any oxygen in the argon and carbon monoxide, these gases were passed through a heated silica tube filled with copper turnings. The argon and carbon monoxide were stored in cylinders under pressure while the air was forced through the fur-

nace under slight pressure after the moisture was removed in the drying towers. Later, moist carbon monoxide and moist air were prepared by bubbling the gases through a water tower. No attempt was made to determine precisely the water vapor content but it was estimated to be of the order of 5 per cent by volume at 100 degrees Fahr.

For the heat treatments, a laboratory type electric furnace heated by silicon carbide resistors was fitted with a sillimanite muffle 30 inches long and an internal diameter of 0.875 inches. A bent tube

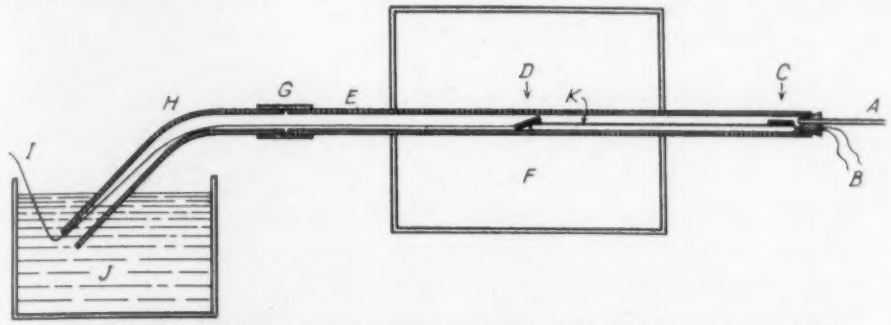


Fig. 19—Apparatus for Special Heat Treatments in Gaseous Atmospheres.
A. Glass Tube Leading to Gas Supply.
B. Leads to Potentiometer.
C. Position of Specimen Before Heating.
D. Position of Specimen Before Quenching.
E. Sillimanite Tube.
F. Resistance Furnace Heated by Silicon Carbide Elements (Not Shown).
G. Rubber Tubing Coated with Shellac.
H. Glass Tubing.
I. Nichrome Wire Attached to Specimen.
J. Oil Quenching Bath.
K. Thermocouple Enclosed in Sealed Sillimanite Tubing.

of pyrex glass was attached, by means of a rubber coupling, to one end of the muffle extending about six inches beyond the end of the furnace. The lower part of the glass tube was immersed in a bath of quenching oil. The specimen, located at the beginning of the experiment at the cold end of the muffle projecting outside of the furnace, was pulled by means of a nichrome wire first to the preheating zone, then to the central zone in contact with a thermocouple, and finally into the quenching bath (see Fig. 19). The system was tested prior to each treatment by raising the oil level in the glass tube and closing all gas connections. Under these conditions, it was found that the oil in the tube remained for several hours above the oil level in the tank. Under this arrangement the specimens moved through the heating zones into the quench without coming into contact with extraneous gas. The furnace temperature, maintained for some time at the desired temperature, dropped about 25 degrees when the speci-

Table IV
Effect of Furnace Atmospheres on Grain Diameter (Microns)

Temperature Degrees Fahr.	Argon	Dry CO	Moist CO	Dry Air	Moist Air
2050	....	....	....	....	4.5
2100	....	....	4.1	....	7.5
2150	....	....	6.0	7.1	12.5
2200	5.0	5.0	7.0	8.3	17.0
2250	7.5	7.5	10.0	11.0	25.0*
2300	11.0	15.0	20.0	16.0	33.0*
2350	14.0	22.0*	33.0*	25.0*	....
2400	33.0*	33.0*	....	40.0*	....

*Incipient melting observed.

men (1.5 × 0.065 inch) was drawn into the furnace. Within twenty seconds the thermocouple (touching the specimen but insulated from the sillimanite tube) registered the original temperature. All of the specimens were heated for a total time of 120 seconds in the high temperature zone where it is believed that all were held at a constant temperature for at least 90 seconds.

Considerable difficulty was experienced with the thermocouples in the argon and carbon monoxide treatments. While every reason-

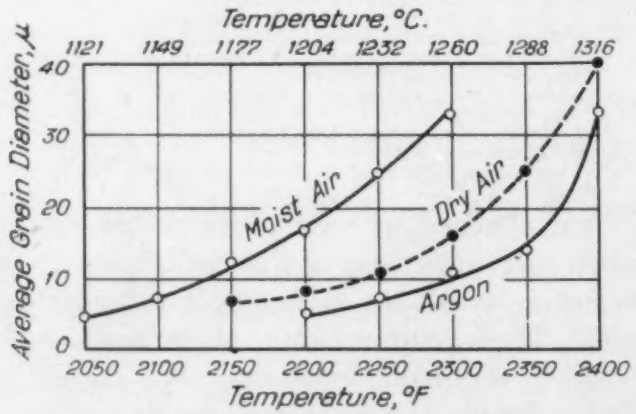
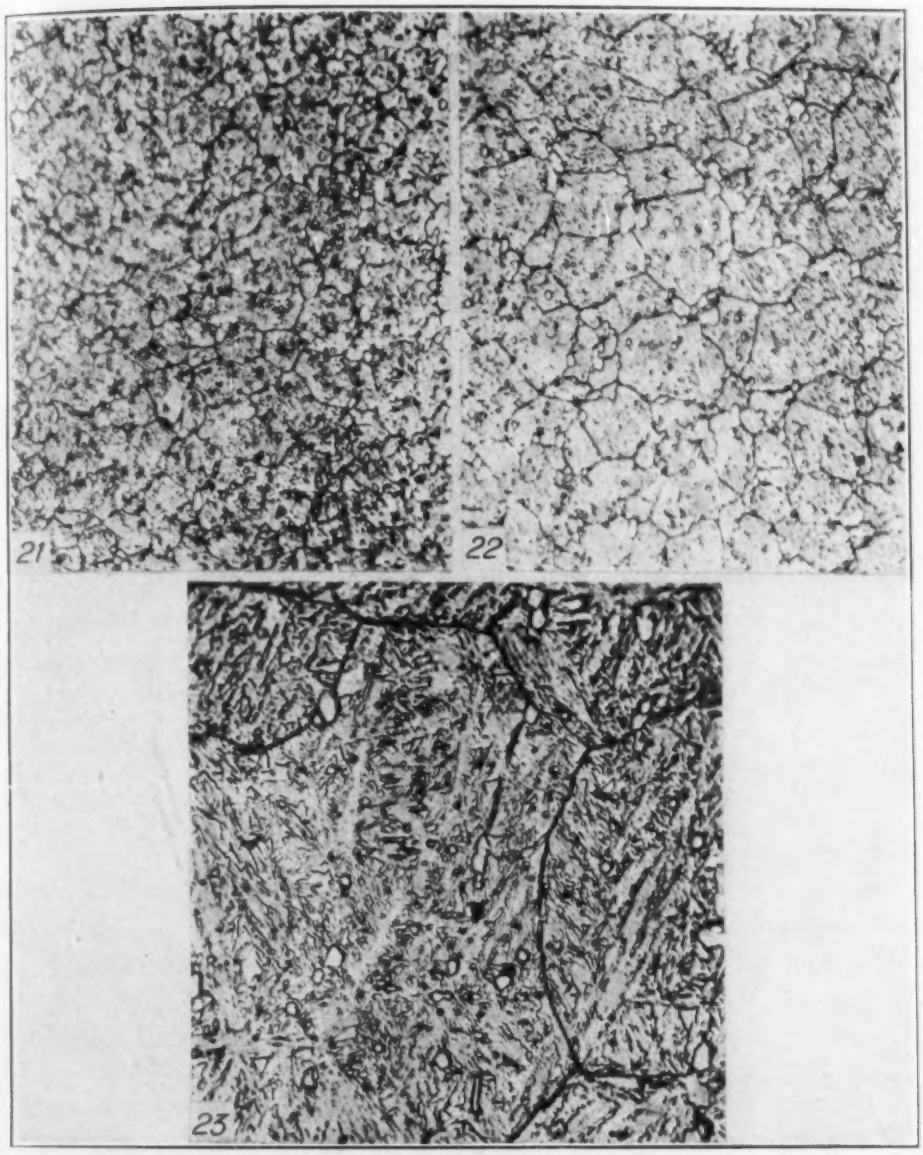


Fig. 20—Graphs Showing Grain-Size Measurements After Heat Treatment in Various Gaseous Atmospheres.

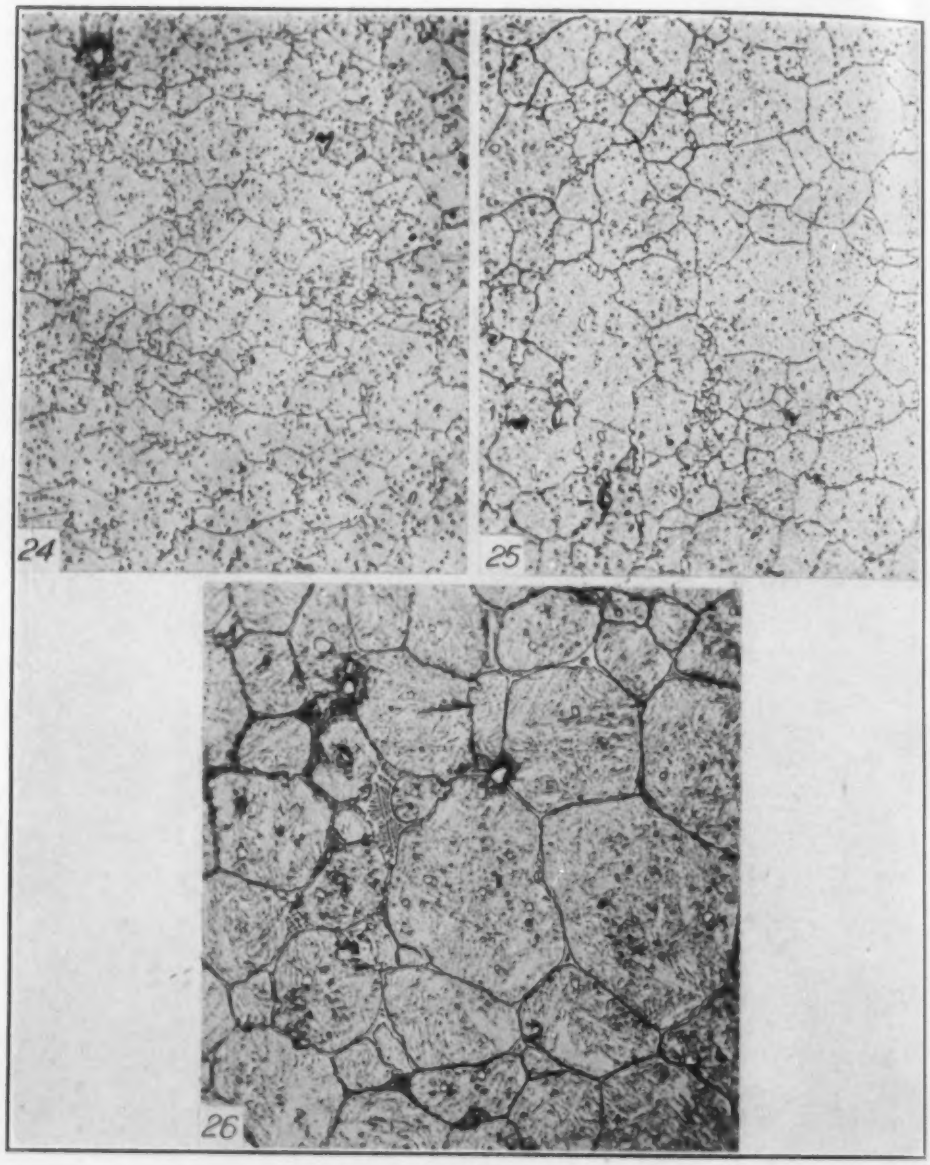
able precaution was taken to secure gas-tight protective coverings for the couple, the wires nevertheless became contaminated and unreliable after about the third heat treatment. This condition necessitated rigid checking of the couples before and after each experiment.

The quenched specimens were prepared for metallographical examination in the manner previously described. Grain-size measurements are summarized in Table IV and plotted in Fig. 20. It is



Photomicrographs of 7 Per Cent Molybdenum High Speed Steel After Being Subjected to Various Gaseous Atmospheres at 2200 Degrees Fahr. (1205 Degrees Cent.). Fig. 21—Argon Atmosphere Used. Fig. 22—Dry Carbon Monoxide Atmosphere Used. Fig. 23—Moist Air Atmosphere Used. All Specimens Etched in 5 Per Cent Nital. × 1000.

interesting, but perhaps not surprising, to note that argon-treated specimens had the smallest average grain-size for all temperatures. At the higher temperatures 2300 and 2350 degrees Fahr. (1260 and 1290 degrees Cent.) the grain-size of the material heated in carbon monoxide was larger than in the argon treatments at the same tem-



Photomicrographs of 7 Per Cent Molybdenum High Speed Steel After Being Subjected to Various Gaseous Atmospheres at 2250 Degrees Fahr. (1230 Degrees Cent.).
Fig. 24—Argon Atmosphere Used.
Fig. 25—Atmosphere of Dry Air Used.
Fig. 26—Atmosphere of Moist Air Used.
All Specimens Etched in 5 Per Cent Nital. × 500.

peratures. At 2400 degrees Fahr. (1315 degrees Cent.) both atmospheres produced the same grain-size although in each case incipient melting was noted. As previously observed, melting at the grain boundaries restricts further grain growth. Relatively coarse grains were obtained in the specimens in contact with dry air. The treat-

ments in air containing water vapor, however, produced the largest grains for any temperature up to that causing local melting. Similarly, water vapor in the carbon monoxide had a distinct coarsening effect.

Typical microstructures produced by heating at 2200 degrees Fahr. (1205 degrees Cent.) in three atmospheres are shown in Figs. 21, 22 and 23. The structure shown in Fig. 23, while not entirely representative of the grain-size of this specimen, illustrates the mag-

Table V
Rockwell Hardness (45 N Scale) on Material After Heat Treatment in Several Atmospheres

Temperature Degrees Fahr.	Argon		Dry CO		Moist CO		Dry Air		Moist Air	
	A*	B†	A*	B†	A*	B†	A*	B†	A*	B†
2100	72.0	72.5	....	....	72.0	70.0	....	....	42.0	70.5
2150	69.0	69.0	72.5	71.0	72.2	72.2	65.0	69.0	21.0	70.0
2200	71.0	71.5	72.5	71.5	71.5	70.0	68.5	70.5	22.0	71.0
2250	71.5	71.7	71.0	70.0	[illegible]	72.5	68.0	70.0	42.0	71.0
2300	72.2	72.0	69.5	71.0	69.0	69.0	69.0	71.0	24.0	71.0
2350	70.5	70.5	69.0	69.5	66.5	71.5	65.0	70.0	....	....

*A readings taken on the "as quenched" material.
†B readings taken on same specimens after grinding.

nitude of the growth resulting from the moist air atmosphere. Figs. 24, 25 and 26 show the relative differences for heat treatments at 2250 degrees Fahr. (1230 degrees Cent.). At this temperature, specimens heated in moist air showed unmistakable evidence of melting although the material exposed to argon and carbon monoxide developed normal structures at the same temperature.

It was observed that the steels heated in argon, dry air and dry carbon monoxide showed no visible evidence of scaling or decarburization. The latter condition was confirmed by a microscopic examination. In the cases of the specimens treated in the presence of water vapor, the surfaces were badly scaled and microscopic study indicated that considerable decarburization had taken place. In order to check the surface conditions more thoroughly, hardness tests were made on the specimens with a Rockwell superficial tester using the fine diamond point and a 45-kilogram load (15 N scale). The tests were applied to the surfaces in the "as-quenched" state and also after grinding the samples on both sides to a depth sufficient to remove any soft skin. The results are assembled in Table V. It is evident that the argon-treated material was absolutely free from a soft skin effect. The very slight hardening suggested by the results obtained

on some of the specimens heated in contact with dry carbon monoxide may possibly be attributed to slight carburization, although no such evidence was found by microscopic examination. On the other hand, the material hardened in an atmosphere of dry air showed an external hardness somewhat less than the sub-surface value. This difference is probably due to loss of carbon at the surface although, again, no microscopic evidence of this condition was revealed.

The reasonably comprehensive metallographical study thus far recorded indicates that furnace atmospheres exert an effect on the grain-size of high molybdenum steels heated to within the temperature range necessary for the proper hardening of this steel. It is evident that grain growth is promoted by oxidizing atmospheres, particularly those containing an appreciable concentration of water vapor. Furthermore, the presence of water vapor in carbon monoxide encourages grain growth; as a matter of fact, at the higher temperatures the grain-size developed in moist carbon monoxide was larger than that developed in dry air.

The mechanics of the structural changes produced by the presence of water vapor are not clearly understood, especially in regard to its effect on the grain-size of the metal well below the visible evidence of decarburization. It is, of course, a matter of general knowledge that the oxidation of metals at ordinary temperatures is greatly accelerated by moisture. Pilling and Bedworth (6) have suggested that high temperature oxidation may be regarded as a form of metallic corrosion. This viewpoint, while accounting for the surface changes, fails to explain the grain-size effects characteristic of the sub-surface material, unless it is assumed that concentration changes take place well below the obvious zone of decarburization. Although preliminary work has indicated that this assumption is not justified, a more rigorous investigation of the concentration gradient is planned. It is possible that, under the conditions of the heat treatments described, water vapor is decomposed, yielding hydrogen and oxygen in the atomic state. This view may be considered untenable on the basis that the dissociation of water vapor at the temperatures involved is negligible. However, little is known regarding the dissociation constant of water vapor in contact, at high temperatures, with a highly reactive surface. Finally the question may be disposed of, but not answered, by stating that the water vapor acts as a catalytic agent.

Grossmann (7) has written rather convincingly regarding the

effect of dissolved oxygen in steel, particularly with respect to its effect on carbide structure and solution. According to his studies oxygen is absorbed in steel under carburizing treatments and the dissolved oxygen increases the solubility of cementite (carbon) in ferrite. In discussing Grossmann's paper, Herty suggested that oxygen, instead of actually increasing the solubility of carbon, merely increased the rate of diffusion. Merica (8) offered the suggestion that oxygen may actually decrease the solubility of cementite in ferrite at low temperatures thereby leading to a precipitation of cementite at low temperature treatments with the resulting condition known as temper brittleness. In this connection Oberhoffer (9) stated that he had convincing evidence pointing to the conclusion that temper brittle steels contained more oxygen than the non-brittle steels, irrespective of other elements present. Schenck (10) reported that iron at high temperatures absorbs large amounts of oxygen, although his analytical results have been questioned by several investigators. It is hoped that reliable data regarding the solubility of oxygen in molybdenum high speed steel will be obtained very shortly as a result of the studies now being carried on in connection with the present investigation. If dissolved oxygen is accepted tentatively as the main factor to be considered in accounting for the unusual grain growth at high temperatures, there is still the necessity of explaining the mechanism of its action in this respect. If one assumes that dissolved oxygen increases the solubility of carbides in austenite, the marked grain growth may be explained on the basis of the removal of particles tending to obstruct grain growth. It is certainly true that the coarse grains developed at the higher temperatures contain fewer visible particles of carbide than the smaller grains developed at the same temperature under neutral or less oxidizing conditions.

Similar reasoning may be applied in accounting for the incipient fusion noted under oxidizing conditions at temperatures lower than that required to produce evidences of melting in material in contact with neutral atmospheres. It was noted that with increasing temperatures, the carbides were absorbed within the grains and that fusion started at or adjacent to the residual carbides found in the grain boundaries which are probably regions of high oxygen concentration. The increased solubility of the carbides in the presence of oxygen would, of course, necessitate some phasial modification, but unfortunately too little is known of the fundamental constitutional relationships of this complicated alloy system to warrant a

precise statement of the changes involved. However, the solid solution thus enriched in carbon (and other elements depending on the nature of the carbides) may form an eutectic with the remaining carbides.

In referring to Tour's (11) results on atmospheric effects on 18 per cent tungsten steel, Gill (12) attributed growth in oxidizing atmospheres to self-heating. In other words, the exothermic reaction associated with the oxidation of the surface and at the grain boundaries of the specimens raised the temperature of the material above the temperature of the furnace, thereby promoting additional grain growth. Jominy (13), (14) has studied this effect in plain carbon steels and found that a strongly oxidizing and turbulent furnace atmosphere produced marked self-heating (about 75 degrees Fahr.) in low carbon steels heated above 2475 degrees Fahr. (1355 degrees Cent.). In no case was self-heating found at temperatures below this point and no instance was found in high carbon steels. In the latter case, grain boundary melting took place according to Jominy, before the temperature necessary for a strong exothermic reaction was attained.

Although the writers did not believe that self-heating was an important factor in the present investigation, it was obvious that the possibility should not be ignored nor dismissed until specific evidence on this question was obtained under the conditions maintained during the former tests. The only departure from the original experiments was the use of material 0.375 inch square and 1.5 inches long. The larger cross section permitted the drilling of a hole, 0.10 inch in diameter, for the insertion of a thermocouple for measuring accurately the maximum temperature attained by the steel. A second couple measured the temperature of the atmosphere immediately surrounding the specimen. In no case did the temperature of the steel rise above that of the furnace, although in one experiment oxygen containing moisture was passed through the furnace. On the basis of the results of several tests conducted in this manner, it is believed that self-heating is of little or no importance in promoting grain growth and low temperature melting of molybdenum steels.

The writers wish to acknowledge the assistance of F. C. Rees, a graduate student in the Department of Metallurgy, for his contribution to the experimental work of this paper.

Bibliography

1. L. Guillet, "Recherches sur les aciers au molybdene," *Revue de Metallurgie Memoirs,* Vol. 1, 1904, p. 390.
2. F. W. Taylor, "On the Art of Cutting Metals," *Transactions,* American Society of Mechanical Engineers, Vol. 28, 1907, p. 31.
3. L. B. Richie, "Molybdenum in High Speed Steels," *Army Ordnance,* Vol. 11, 1930, p. 13.
4. J. V. Emmons, "Some Molybdenum High Speed Steels," TRANSACTIONS, American Society for Metals, Vol. 21, 1933, p. 193.
5. Grossmann and Bain, "High Speed Steel," John Wiley & Sons, Inc., New York, 1931.
6. Pilling and Bedworth, "Oxidation of Metals at High Temperatures," *Journal,* Institute of Metals, Vol. 29, 1933, p. 529.
7. M. A. Grossmann, "On Oxygen Dissolved in Steel and its Influence on the Structure," TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 1.
8. P. D. Merica, Discussion of paper by M. A. Grossmann (loc. cit.).
9. P. Oberhoffer, see above discussion by P. D. Merica.
10. R. Schenck, "Gleichgewichtsuntersuchung über die Reduktions—Oxydations —und Kohlungsvorgänge beim Eisen—IV," *Zeit. für anorg. Chemie,* Vol. 167, Parts 1 and 2, 254, 1927.
11. S. Tour, "The Temperature Atmosphere Problem in High Speed Steel," TRANSACTIONS, American Society for Metals, Vol. 21, 1933, p. 269.
12. J. P. Gill, "Tool Steels," Series of Lectures presented before American Society for Metals, at National Metal Congress, New York, 1934, (p. 123).
13. W. E. Jominy, "A Study of Burning and Overheating of Steels, Part I," TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 298.
14. W. E. Jominy, "A Study of Burning and Overheating of Steels, Part III," TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 893.

DISCUSSION

Written Discussion: By Sam Tour, Lucius Pitkin, Inc., New York City.

It was indeed a pleasure to be permitted to study this paper in advance of its presentation. It is desired to compliment the authors highly on the thorough and painstaking work represented by this paper and the clarity with which the material has been presented, as well as the forcefulness of the experimental data obtained in support of their conclusions.

In 1930 the writer first published ("The Heat Treatment of Delicate Tools of High Speed Steel"—*Fuels and Furnaces,* September, 1930) an article giving actual data indicating that during the heating of high speed steel for hardening there is a difference in the extent of grain growth according to the type of atmosphere in the furnace. In 1932, the writer offered further results of studies on the standard 18-4-1 high speed steel ("The Temperature Atmosphere Problem in High Speed Steel"—TRANSACTIONS, American Society for Metals, Volume 21, 1933). In the interim between these two papers the writer had occa-

sion to speak to a number of the chapters of the American Society for Metals in various parts of the country, and in these talks pointed out that this phenomenon of an oxidizing atmosphere causing rapid grain growth in 18-4-1 high speed steel at temperatures around 2300 and 2400 degrees Fahr. (1260 and 1315 degrees Cent.), did not occur with all steels. The writer showed, by way of specific example of this, that it did not apply in the case of a 26 per cent chromium iron. In these talks it was invariably suggested that combusted gas atmosphere containing around 10 to 11 per cent carbon monoxide should be used for the high temperature treatment of 18-4-1 high speed steel, although in the paper presented in 1932 no such specific recommendation was made.

The writer noted particularly the statements made by J. P. Gill in the series of lectures on Tool Steels presented before the American Society for Metals in 1934 as follows:

"It therefore appears that the atmosphere in itself has no influence on either the rate of growth of austenitic grain or upon the fusion point of the segregate so long as it does not change the composition of the steel by carburizing or decarburizing. The gas indirectly affects the size of the austenitic grain only as it affects the temperature of the specimen."

This rather easy explanation of a somewhat obscure phenomenon has not been borne out by experiments carried out by others. It has been found that specimens heated in a furnace in a reducing atmosphere sometimes do not reach the full indicated temperature of the furnace. It has been found that specimens heated in a furnace with a strongly oxidizing atmosphere do sometimes reach temperatures higher than the furnace temperature indicated by the furnace pyrometer. The writer has been advised of tests carried out in which the furnace was maintained at a lower temperature when the oxidizing atmosphere was used and at a higher temperature when the reducing atmosphere was used with a thermocouple touching the specimens so that actual specimen temperatures were read and actual specimen temperatures maintained the same for the different atmospheres. Metallographic examinations of these specimens so treated have been reported to the writer as showing definitely a larger grain-size resulting from the oxidizing atmosphere than from the reducing atmosphere.

The writer has also had occasion to note statements made by S. K. Oliver in a paper presented at the Tri-Chapter meeting of Dayton, Columbus and Cincinnati chapters of the American Society for Metals, April 15, 1935 ("Hardening Tool Steels in Controlled Atmospheres"—*Steel*, June 24, 1935). In this paper Mr. Oliver attempts to show that an atmosphere which works satisfactorily in one part of the country does not work satisfactorily in another part of the country. Unfortunately, Mr. Oliver took figures for furnace atmospheres from the writer's 1932 paper as used for an experimental heat treatment at 2300 degrees Fahr. (1260 degrees Cent.), and attempted to apply this atmosphere for heat treatment at a much higher temperature. Getting poor results in this attempt, Mr. Oliver then dropped the whole problem without further work. It is difficult, as indicated by the brief tests made and reported by Mr. Gill, and then as in the brief tests made and reported by Mr. Oliver, to obtain results which will check a portion of a much larger program of work previously carried out by some other experimenter. This is probably due to the fact that very few papers describe experiments in sufficient detail to allow of their

being duplicated, with the result that anyone desiring to prove or disprove such an original program of work must necessarily in his new program make tests to practically parallel the entire original program. Apparently this was not done by Gill or Oliver.

It is indeed pleasing to see that Phillips and Weldon have carried out a complete program and have found results similar to those reported by the writer three and five years ago. Phillips and Weldon have worked on a molybdenum high speed steel instead of a tungsten high speed steel. It is felt, however, that their results have amply confirmed the writer's previous results, in addition to having proved that the same phenomenon applies to both the molybdenum type and the tungsten type of high speed steel.

It is suggested to Phillips and Weldon that some analyses as to oxygen, carbon dioxide and carbon monoxide content of the atmospheres which they report as "highly reducing," "slightly reducing," "slightly oxidizing" and "highly oxidizing" be incorporated in their paper. In the first portion of their paper they refer to carrying out of heat treatments in "the well known type of gas furnace containing a vertical carborundum muffle. Three holes in the base of the muffle permitted ready passage of the products of combustion upward through the muffle." This type of furnace is not so well known to the writer, and he would like to inquire whether the high oxidizing atmospheres are obtained in such a furnace by closing up the three holes in the base of the muffle and admitting air from the top, or whether the oxidizing atmosphere is obtained by using a very great excess of air in the combustion chamber. It would also be a distinct and valuable addition to the paper if the authors would describe in some detail what is meant by "follow standard practice with regard to atmospheric conditions." The authors describe some final tests on the subject of "self heating" in which they used specimens ⅜ inch square by 1½ inch long, with a thermocouple inserted in a hole drilled into the specimen. The writer would like to inquire whether in these experiments the authors found a difference in the heating rate of the specimens for the different furnace atmospheres. There is a possibility, and some evidence, that the rate of heating of a specimen placed in a furnace at a given temperature is less in a reducing atmosphere than in an oxidizing atmosphere.

In conclusion, the writer wishes to call attention to the fact that grain growth as affected by furnace atmospheres is of importance in nonferrous metals as well as in steels, but whether grain growth will be promoted or inhibited is a peculiarity of the alloy itself. For example, it seems that oxygen or oxygen-carrying gases promote grain growth in high speed steels, whereas in some nonferrous alloys, oxygen and oxygen-carrying gases seem to inhibit grain growth, while hydrogen promotes grain growth. It, therefore, becomes a specific problem for each alloy and a considerable amount of experimental work and information will be necessary before all of these gas metal problems can be solved or even very well understood.

Written Discussion: By J. P. Gill, metallurgist, Vanadium-Alloys Steel Co., Latrobe, Pa.

The writer has read this paper with considerable interest and the information regarding susceptibility to grain growth in molybdenum high speed steels as affected by different atmospheres is, if we except the differential in temper-

atures, substantially the same as that reported by Mr. Tour on an 18 per cent tungsten high speed steel. There is also a marked similarity between the authors' results and procedure with some of the original work of our laboratory on 18 per cent tungsten high speed steel.

Our experiments indicated that unusual care and technique were required in these investigations. Consequently, I am surprised that the authors used sheet stock approximately only $\frac{1}{16}$ inch in thickness; which sheet stock was hot-rolled with an admitted decarburized surface, possibly a demolybdenized surface and even no statement on their part as to whether or not the "hot-rolled scale" or oxide was removed from the samples. Since surface reactions are so important in the subject under discussion it is most necessary that every precaution be made so that the specimens have a uniform surface representative of the body of the metal and a surface condition which is definitely known. In many experiments which we conducted we often found a much more intense reaction at the surface of the specimen than in the body of the specimen. This zone in some instances being as deep as 0.030 inch. Should specimens have been made of sheet stock only 0.065 inch in thickness, it is obvious in some cases that the zone of more intense reaction would have extended entirely through the specimen.

In Tables II and III the authors mention determination of decarburization by the use of the microscope and while such a method of investigation may serve satisfactorily for a high degree of decarburization, it is impossible in 18 per cent tungsten high speed steels to determine low degrees of partial decarburization by the microscope. In an 18 per cent tungsten high speed steel there is no difference in appearance under the microscope of an area containing 0.70 per cent carbon and an area containing 0.60 per cent carbon.

Several years ago we conducted a number of experiments on an 18 per cent tungsten high speed steel in an effort to determine the effect of gases on grain-size and structure. We used specimens about $\frac{1}{4}$ inch in diameter and $1\frac{1}{2}$ inch in length which had been machined all over. Two different furnaces were used, one a molybdenum-wound electric furnace with a silicon tube. Gases of known composition were premixed and passed over the specimens much in the manner as did the authors. The other furnace was a controlled atmosphere furnace, adjusting the atmosphere in a number of instances to correspond in composition to some of the atmospheres used in the molybdenum-wound furnace. In all cases a thermocouple was placed directly against the specimen. A comparison of the grain-size resulting in specimens treated in different furnaces and using substantially the same atmospheres was not consistent. In investigating the reason for this inconsistency a hole was drilled longitudinally into the specimen and a thermocouple placed in the center. Using this thermocouple for control purposes our results between the two different furnaces were much more consistent but we also found that the different gases had a lesser effect on grain growth than we had originally assumed. It was found that in using so-called highly reducing atmospheres the specimens did not come to temperature as rapidly as when using so-called highly oxidizing atmospheres and that in several cases where oxygen had been introduced into the atmosphere the specimens became hotter than the furnace temperature.

Since grain-size is affected by both time and temperature, we found that by

adjusting the furnace temperature so that the specimens would come to temperature in approximately the same length of time, the atmosphere, whether reducing or oxidizing, would not then greatly affect the grain-size.

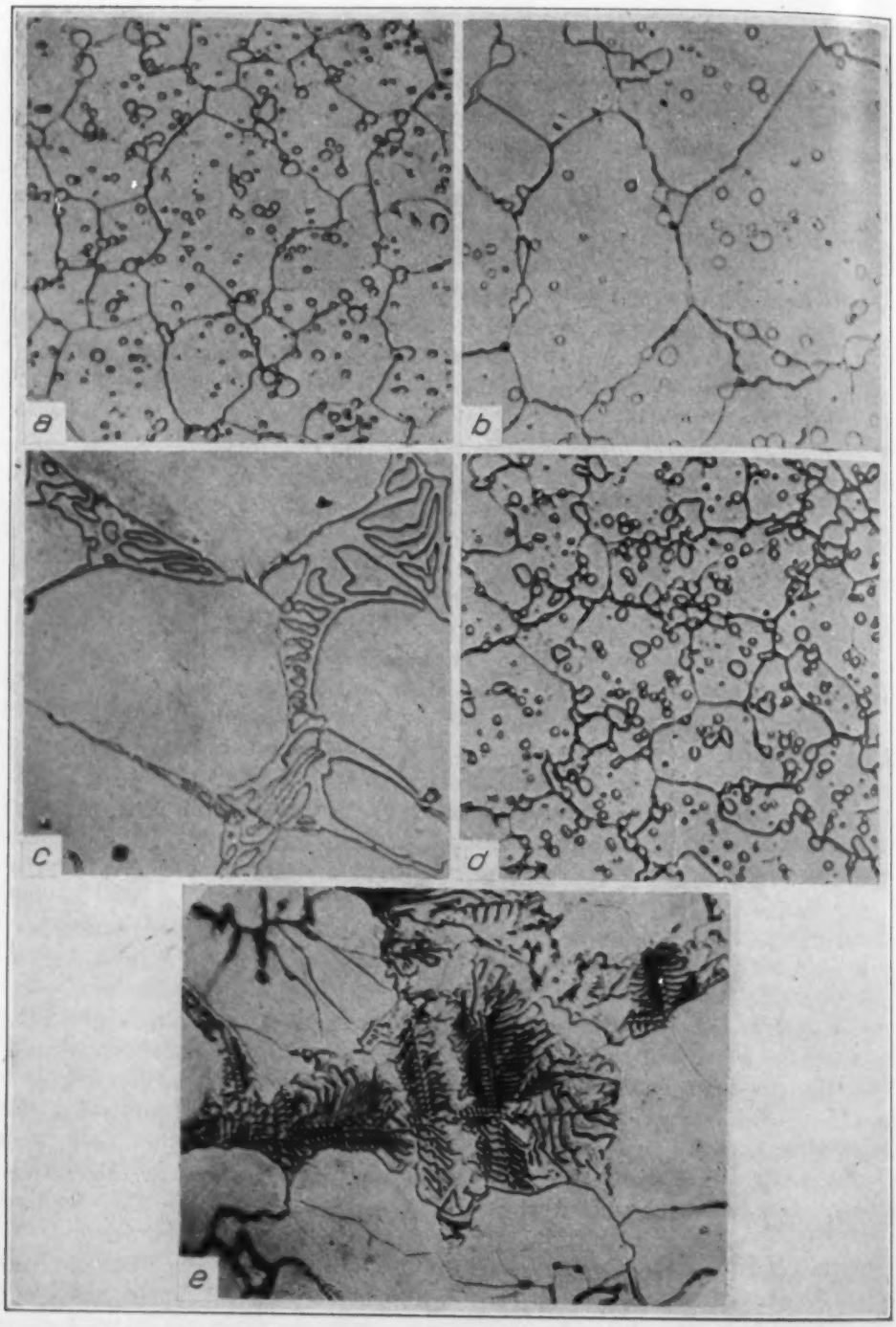
The authors make mention of one specimen which they tested in a highly oxidizing atmosphere and state that the thermocouple in the specimen and the furnace were the same which is undoubtedly correct, but they have not made any statements as to the rate at which the specimens might come to temperature using different atmospheres. This rate, of course, affecting the length of time the specimens would be at temperature when all of them were held in the furnace the same length of time.

From the experiments which we made we concluded that apparently so long as the gases surrounding the specimen were not affecting either carburization or decarburization of the steel that apparently the gases themselves would not affect grain growth to the extent that some investigators had assumed, other than as they may affect the temperature and rate of heating of the specimen.

The authors held their specimens in the furnace a total time of 130 seconds. When a grain as large as that shown in the authors' figures from 11 to 14 inclusive will result in such a length of time, it is apparent that changing the length of time at temperature only a few seconds would noticeably change the grain-size. The authors have shown two photomicrographs, namely, Fig. 17 and Fig. 18, which are assumed to have been heated to the same temperature, one in a reducing and the other in an oxidizing atmosphere. In Fig. 18 it is obvious that the segregate has fused but a close examination of Fig. 17 will show that fusion was beginning in the segregate. The authors have offered their theory as to why atmospheres may affect grain growth and granting the plausibility of such theory as affecting grain-size, I do not see how such a theory could in any way be applied to the fusion of the segregate. The segregate which fuses in an 18 per cent tungsten high speed steel is of the same composition in both the hardened and annealed state. This has been indicated by both X-ray patterns and chemical composition. X-ray patterns also indicate this is true for a molybdenum high speed steel. It would seem most difficult to believe that in a total time of 130 seconds a solid under practically atmospheric pressures could absorb or transfer a sufficient amount of gas to actually lower the fusion temperature of the segregate imbedded within it. Time and temperature offer the simple explanation of the phenomena observed and I do not believe that the authors' experiments have been conducted in a manner to disprove this explanation.

Written Discussion: By R. M. Brick, research assistant, Yale University, and Frank Garratt, technical director, Universal Steel Co., Bridgeville, Pa.

The effect of furnace atmospheres on the structure and properties of steels is of considerable theoretical interest as well as of practical importance. The data published by the authors will be significant to the increasingly large number of metallurgists using the newer molybdenum tool steels. It now seems certain that oxygen, and also water vapor, when present in the furnace atmosphere, affect the inner structure of molybdenum tool steels as well as contributing to the recognized "soft skin" formed on unprotected surfaces. Some



Figs. a to c—MoTung High Speed Steel. Figs. d and e—High Speed Steel of the 18-4-1 Type. × 1000. See Accompanying Table for Description of Photomicrographs.

work has been performed by the writers in an attempt to define the mechanism of the action of oxygen in increasing grain growth and lowering the incipient

melting point. The steel used, MoTung, is similar to that employed by the authors except that a portion of the vanadium is here replaced by a certain amount of tungsten. Three-quarter-inch rods of this material were hardened at the Universal Steel Company in Bridgeville, Pa., under the reducing and oxidizing conditions shown in the accompanying table. The time at the hardening temperature was varied sufficiently to give the three desired structures,

Microstructure No.	(a)	(b)	(c)	(d)	(e)
Specimen	MT 1	MT 2	MT 3	HS 1	HS 2
Structure	Normal	Coarse	Burnt	Normal	Burnt
Preheat—	1250	1250	1250	1550	1550
Degrees Fahr.					
Hardened—	2200	2200	2200	2360	2375
Degrees Fahr.					
(Minutes)	1	2	5	1	1
Atmosphere	Reducing	Oxidizing	Oxidizing	Reducing	Oxidizing
CO %	13.8	0.2	0.2	13.4	0.0
CO_2 %	2.6	1.2	1.2	2.8	0.6
O_2 %	1.0	19.4	19.4	0.8	19.8
Quench	Oil	Oil	Oil	Oil	Oil
Gas Analysis					
O_2 %	0.0043	0.0034	0.0045	0.0091	0.0096
H_2 %	0.0001	0.0000	0.0001	0.0001	0.0000
N_2 %	0.0165	0.0162	0.0187	0.0173	0.0161

shown in the figure—normal fine-grained, coarse-grained, and partially melted. Similar specimens of the usual 18-4-1 high speed steel were also prepared. The outer surface of the specimens was ground away to the point where the rod had its representative structure. Complete gas analyses, in duplicate, were then made of the specimens employing a vacuum fusion set-up very similar to that designed by L. Reeve, (American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1934, Vol. 113, p. 82). This equipment has been checked and found to give results consistent with other analyses on a Bureau of Standards specimen.

The oxygen contents of the steels, shown in the table, are nearly identical and seem to indicate that oxygen does not remain in the steel nor apparently does it participate in the eutectic formed in over-heated MoTung. The mechanism of the effect of oxygen and water vapor in the furnace atmosphere on grain growth and eutectic melting remains obscure. The authors seem to have disposed, in their work at least, of the suggestion of "self-heating" being responsible or of the possibility of oxygen affecting the rate of heat transfer. The fact that at a fairly low hardening temperature, eutectic melting will take place in an oxidizing atmosphere and not in a reducing atmosphere strongly suggests a change in composition of the steel to a position above a solidus line. This shift in composition is apparently not accompanied by an oxygen pick-up. The most logical surmise would be that there is a loss in carbon, by the diffusion of monatomic oxygen through the steel, the formation of CO and the subsequent diffusion out of the steel of the CO. The effect of water vapor on this basis may be explained by assuming that the reactive surface of the steel dissociates the water vapor, supplying more monatomic oxygen which would quickly enter the steel while the hydrogen would be removed by convection currents. No completely reliable data is at hand to disprove this suggestion.

The Universal Steel Company found that a 2½-inch billet of Mo Tung held 10 hours at 2100 degrees Fahr. (1150 degrees Cent.) lost only 0.005 per cent carbon (an average of 12 analyses), but this temperature is lower than those employed for hardening, the composition of the furnace atmosphere was not definitely known, and the analyses were made near the center of a thick section.

Oral Discussion

E. E. THUM:[1] Since the work which was done by Mr. Oliver at Delco Products Corp. on tool steel and described by him before the Tri Chapters a year or so ago has been mentioned, it might be in order to record some observations made there at a recent inspection trip. Without wishing to stand as his personal representative, it will be well to repeat his warning that results obtained in a laboratory furnace under precise control may have little apparent relation to the output of a production furnace. The burden of Mr. Oliver's talk at that meeting was that he had fooled himself so many times with laboratory results that he always puts a question mark after any statement about practical heat treatment based on such work.

The reason this is so is fairly clear. Take an electrically heated furnace for high speed steel, for example, and introduce into it a certain mixture of gases which may be carefully prepared and in equilibrium when it leaves the preparation unit. On entering the furnace it meets suddenly a very hot electrical resistor, hot brick walls and hearth, and, say, cool metal. None of these is at the temperature wherein the gas is in equilibrium. Likewise, as the temperature of the metal increases, the conditions of equilibrium at its surface continually change. How, then, can anyone take a gas analysis from such a furnace at any time and say—"That is the atmosphere, and these are its effects"?

The whole problem of controlled atmosphere in heat treating is related to the questions discussed by Messrs. Phillips and Weldon. Atmospheres can be produced in practice that will oxidize, others that will decarburize, others that will carburize, and still others that will do various combinations of these things at different rates. The commonest paradox is found by packing a high carbon tool steel in carburizing material, bringing to heat and quenching; the tool will have a soft skin as much as 0.010 inch deep. The practical cure is to scale off this soft skin as fast as it forms. A strictly *neutral* atmosphere containing oxygen, if possible theoretically, requires such delicate adjustment that it is impossible to achieve in practice.

Mr. Oliver tells me that the best results he has been able to get with the type of tool steel described by the authors has been to preheat at 1600 degrees Fahr. in an "oxidizing" atmosphere (nominally 1 per cent CO and 7 per cent CO_2) and harden from 2150 degrees Fahr., the high heat furnace operating with a "reducing" atmosphere (nominally 9.2 per cent CO and 3.4 per cent CO_2). The furnaces are the Hayes "certain curtain" type, electrically heated. The tools scale 0.0008 to 0.001 inch, but there is no soft skin. In a tube type of furnace, where gas and metal both progress from cooler to hotter regions

[1]Editor, *Metal Progress*, 7016 Euclid Ave., Cleveland, Ohio.

up to the quenching point, this steel has been hardened without measurable scale or soft skin.

In his opinion, time and temperature are the controlling major factors in grain growth.

Authors' Closure

The authors acknowledge with pleasure Mr. Tour's discussion which related his observations with respect to furnace atmospheres on the standard 18-4-1 high speed steel. It is indeed interesting to note the similarity of results obtained by Mr. Tour and the writers on the two types of high speed steel. Obviously, much remains to be done before our knowledge of atmosphere effects is sufficiently complete to enable us to formulate the optimum procedure for heat treating the structurally complex alloy steels of today.

In answer to Mr. Tour's question regarding the analyses of the furnace gases reported as "slightly oxidizing" etc., it can only be stated that these heat treatments were carried on in an industrial unit and no chemical analyses of the furnace gases were obtained. The object of this experiment, regarded as a preliminary step in the investigation, was to obtain general information regarding the significance of the atmosphere variations which are commonly encountered in industrial practice. The modifications in gas conditions referred to were affected by regulation of the air input in the combustion chamber and not by opening and closing the holes in the base of the muffle.

Mr. Thum's remarks regarding the danger of applying the results obtained in a laboratory furnace to industrial hardening practice are fully appreciated by the writers. This realization, however, ought not lead to a deprecation of laboratory experimentation in this field but merely emphasizes the fact that discrepancies in results are usually due to troublesome and sometimes unavoidable complications associated with the use of production units.

The authors are particularly interested in the experiments reported by Messrs. Brick and Garratt. The gas analyses included in their discussion were undertaken by Dr. Brick in the Hammond Metallurgical Laboratory but were completed too late to be incorporated in the original paper. Apparently Dr. Brick's results eliminate the probability of an oxygen pick-up as the explanation of the effects described.

Mr. Gill's criticisms are largely based on the results of his study of atmosphere effects on 18 per cent tungsten high speed steel. The authors noted references to this work but when writing the paper were unable to locate any detailed account of his investigation. Mr. Gill's statement concerning the use of sheet steel for a study of this kind is to some extent justified. However, it may be said that the original plan was initiated by an industrial research which necessitated the use of sheet steel of the gage specified. Furthermore, the study of specimens in the hot-rolled condition with unground surfaces was also demanded by the stipulation that the product must be hardened without a prior grinding of the surfaces. However, the sheet was carefully processed, using borax protection, with little surface alteration. Moreover, supplementary work on ground samples yielded results in line with the data submitted in the paper.

The most important feature of Mr. Gill's discussion is the contention that

the grain-size effects reported by the authors may be attributed to time and temperature factors. This explanation, while admittedly not entirely eliminated by the experimental works of our paper, cannot be accepted by the authors without more convincing evidence. In the first place, careful observations indicated no significant differences in the times required for specimens in the several atmospheres to attain the effective hardening temperatures. The specimens of small cross sectional area, reached the hardening temperature in a very short time and any differences in heating rates were too slight to be noted. Assuming, however, differences of a few seconds we are inclined to question the significance of this variable in accounting for the marked grain-size differences found. At a temperature of 2300 degrees Fahr. (Fig. 20) a specimen heated in moist air developed a grain diameter three times that of a specimen similarly heat treated in an atmosphere of argon. We cannot believe that a 3 to 1 grain-size ratio can be explained on the basis of differences in heating rates too slight to be observed by ordinary methods. A consideration of Fig. 9, showing grain-size as a function of time at temperature, also seems to preclude the possibility of the time factor as an important variable in this respect.

In conclusion we would welcome more convincing evidence that furnace atmospheres markedly influence the rate of heat absorption by the specimen. From the standpoint of the relative specific heats of furnace gases it is quite possible that unusual ratios of specimen volume to gas volume might lead to heating rate differences. Under normal conditions, however, in which the specimen volume is very small in comparison with the gas volume we believe that further evidence must be obtained in this respect before we can accept Mr. Gill's explanation of the grain-size and fusing point characteristics of the specimens described in our paper.

CORRELATION OF FAILURES FROM EMBRITTLEMENT OF 4 TO 6 PER CENT CHROMIUM STEEL WITH THE NOTCHED BAR IMPACT TEST

By H. M. Wilten

Abstract

Chromium steel tubes of the 4 to 6 per cent chromium type when used in refinery cracking stills in the form of coils are subject to embrittlement. This embrittlement was found to agree with the laboratory temper brittleness test. Steel that is temper brittle is subject to brittle failures. Steel that is not temper brittle has not suffered brittle failures in service. The temper brittleness phenomena may not be accompanied by the precipitation. Service data supporting this opinion are presented.

Introduction

THE purpose of this paper is to discuss the significance of notched bar impact test with respect to failures of 4 to 6 per cent chromium steel in oil refinery service as a result of embrittlement, and to study the nature of this embrittlement. In the particular use of 4 to 6 per cent chromium type steels in the oil refinery, the notched bar test, and, particularly, the purely laboratory temper brittleness test, evaluates the comparative quality of these steels for this service in a very practical manner.

The same steels as used in service were subjected to an experimental study of their properties; on different types of aging; at subnormal temperatures; temper brittleness tests; with a view of obtaining more data regarding the nature of the embrittlement suffered by these steels.

Service Conditions of 4 to 6 Per Cent Chromium Type Steels

Chromium steels of the 4 to 6 per cent chromium type find their greatest application in cracking stills. Suitably connected, these steels,

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The author, H. M. Wilten, is associated with the metallurgical department, The Texas Co., Port Arthur, Texas. Manuscript received May 28, 1935.

used in the form of tubes, form a part of the coil of the heater of the cracking still. The cracking unit makes a run of several hundred hours—until forced to shut down, usually due to coke formation in the battery. During the shut down period, the tubes are cleaned of coke and inspected before starting another run. The tube failures of the above steels can roughly be divided into two classes:

1. Normal—due to overheating, mainly due to creep in coked sections; these are principally a result of operating conditions.
2. Abnormal—consisting in splitting of tubes at ordinary temperatures when the heater is not operating. These failures have been previously reported by the author (2).[1]

The typical properties of the tube metal, resulting from each type of failure, are discussed in the following.

Normal Failures Due to Over-heating—Typical failure due to overheating is illustrated in Fig. 1. The original tube was 5 inches O. D. by 3½ inches I. D. Due to creep at high temperature, the tube bulged to $5\frac{5}{16}$ inches and a split resulted near the top end of the tube, at the location of maximum heat density. This tube was in service more than four years. Fig. 1 illustrates, particularly:

1. Thick deposit of coke, showing the severe conditions under which tube occasionally operated.
2. Side away from fire is still ¾-inch thick, showing practically no corrosion taking place.
3. Some metal is lost due to scaling, scale being $\frac{1}{16}$-inch thick on the surface away from the fire, ranging to ⅛-inch thick on the side facing the fire.

On this tube, which analyzed 0.18 per cent carbon and 4.71 per cent chromium, impact tests and laboratory temper brittleness tests, as devised by Greaves and Jones (3), were made. In this method, duplicate samples of the steels to be examined were hardened in water from 1650 degrees Fahr. (890 degrees Cent.) and tempered at 1200 degrees Fahr. (650 degrees Cent.); one sample was cooled in water after tempering and the other was cooled slowly in the furnace. Susceptibility to temper brittleness may be taken as the ratio of the impact figure of the sample rapidly cooled to that of the sample cooled slowly after tempering. The higher the ratio, the more

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

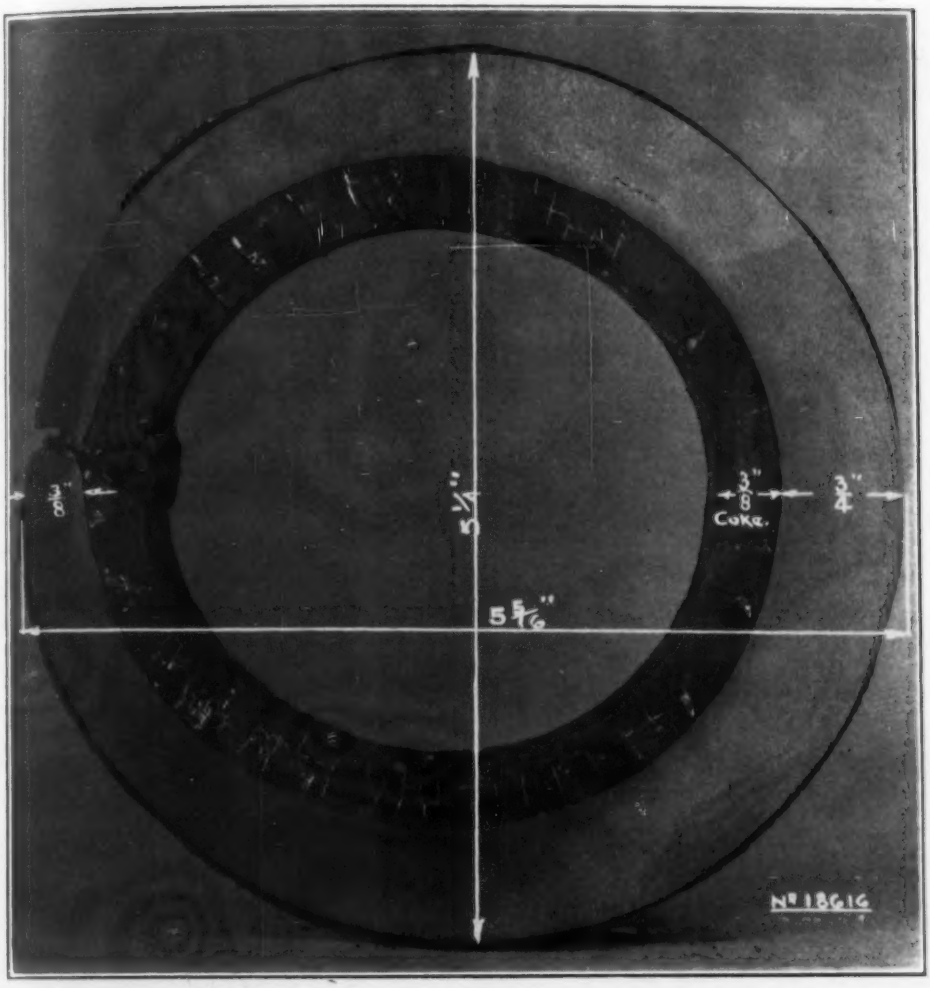


Fig. 1—Section Through a Split Overheated Tube of the 4 to 6 Per Cent Chromium Type.

brittle the material. This test was somewhat augmented by breaking the specimens so treated, not only at room temperature, but also at temperatures lower and higher than ordinary room temperature. Table I shows the data for a typical failure due to overheating. The impact properties of the metal show fair values, although the metal is temper brittle and loses its impact strength rapidly below room temperatures.

Abnormal, Brittle Failures—In contrast to these failures, Fig. 2 illustrates an abnormal failure—a cold split which occurred during the cleaning operation, when the heaters were at atmospheric temperatures. The physical properties of the metal in four typical cases are presented in Tables II to V, inclusive.

A study of the physical properties show:

1. Tensile properties are uniformly good in all sections of tubing.

2. The average Charpy impact of new tubes, keyhole notch, is 46 ft.-lbs. (obtained elsewhere). The average value on four tubes presented here, representing 39 values taken on different sections of these tubes, is 38.4 ft.-lbs. This repre-

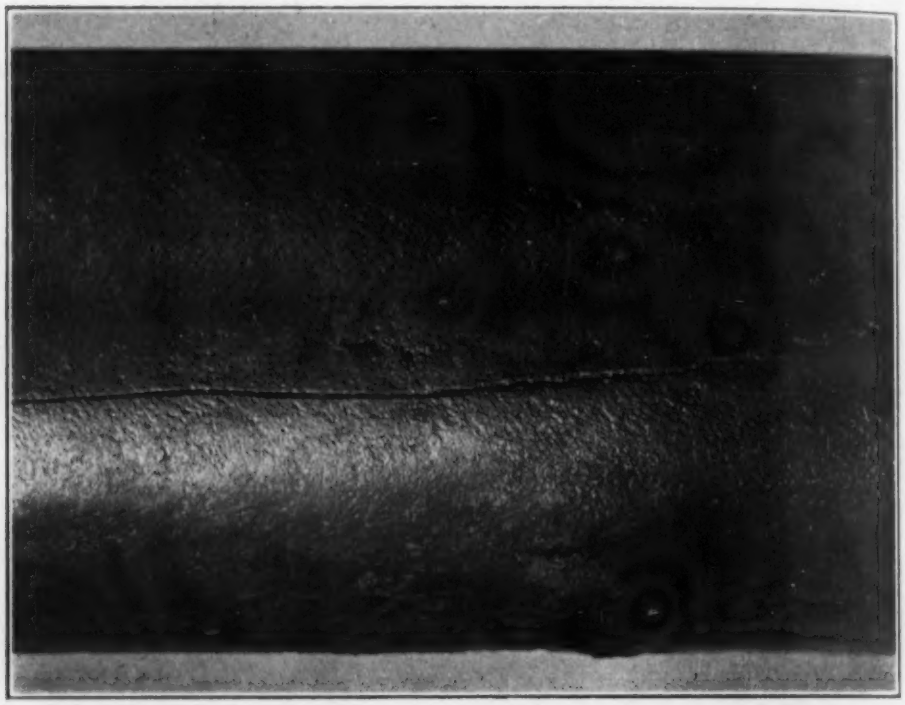


Fig. 2—Split Tube of the 4 to 6 Per Cent Chromium Type Resulting from Embrittlement.

sents a loss of about 16 per cent in impact strength. An entirely different picture presents itself when impact tests with the Izod "V" notch are analyzed. The Charpy impact of new tubes with Izod notch averages 101 (obtained elsewhere); the average value of 38 impact tests, taken from all sections of four tubes, is only 31.5 ft-lbs., which represents a loss of 70 per cent in impact value. If the impact values of only split sections are averaged, this figure becomes 21.5 ft.-lbs., or a loss, from original impact, of some 80 per cent.

3. The variation in impact values with the change in temperature shows a sharp rise when tested at 212 degrees

Table I

Charpy Impact Property of a Tube Which Failed as a Result of Over-Heating

Temperature at Which Tests Were Broken	Charpy Ft.-Lbs.	Temper Brittleness Test	
		Specimens	Charpy Ft.-Lbs.
−40° F. (−40° C.)	11.7	Quenched	110.9
0° F. (−18° C.)	10.7	Furnace-Cooled	18.8
32° F. (0° C.)	12.9	Ratio	5.9
52° F. (10° C.)	38.7		
85° F. (30° C.)	46.7		
212° F. (100° C.)	153.2		

Note 1—Specimens taken from a portion of the tube very near the split.

Note 2—In this and in subsequent cases the notches were cut on the tube thickness surface between the inside and outside surfaces of the tubes. The alternate Charpy specimens with a "V" notch were used in all cases, dimensions being the same as recommended by the A.S.M., except that length was 60 mm.

Note 3—The figures in the table represent an average of at least two values.

Table II

Service Conditions of Split Tubes

Tube Description	Service Life in Years	Metal Operating Temperature Maximum Degrees Fahr.		Operating Pressure of Oil Pounds Per Sq. In.	Occurrence of Split	Carbon Per Cent	Chromium Per Cent
A	2.5	1050	(565° C.)	540	Bottom	0.17	5.06
B	3.5	1050	(565° C.)	900	Bottom	0.17	4.81
C	3.25	1200	(650° C.)	665	Bottom	....	....
D	3.2	1100	(595° C.)	520	Bottom	0.19	4.03

Note: The tubes in this type of the heater were installed vertically.

Table III

Tensile Properties of Split Tubes

Tube Designation	Location of Specimen	Yield Strength Lbs./Sq. In.	Tensile Strength Lbs./Sq. In.	Elongation in 2 In. Per Cent	Reduction of Area Per Cent	Brinell
Tube A	S1[1]	26500	66500	35	77.1	123
	S2	25700	68900	33	74.8	123
	S3[2]	34000	65700	32.5	76.3	123
	T1[3]	32900	65800	34.5	76.7	123
Tube B	S1	32300	62300	32.5	79.5	128
	S2	46300	67700	31.0	77.2	149
	T1	36000	70800	34	79.3	143
Tube C	S1	30500	69600	34	78.4	
	T1	32400	72700	32.5	73.5	
Tube D	S1	.....	79500	36.5	76.6	
	T1	38900	75750	36.5	71.6	

Note 1—Specimens S1 were taken on strips next to the splits; specimens S2 were taken on side diametrically opposite to S1.

Note 2—Specimens S3 were taken on Tube A three feet above the actual split.

Note 3—Specimens T1 were taken near the top of tubes (all tubes in this discussion are installed in vertical position). These portions of tubes are subject to greatest heat density.

Table IV

Impact Properties of Tube Metal Charpy Ft.-Lbs.—Izod Notch

Tube Designation	Location	Temperature of Test 32° F. (0° C.)	75° F. (25° C.)	212° F. (100° C.)	320° F. (160° C.)	Remarks
A	S1	15.5	19.1	57.3	162	Split
	S3	16.8	38.6	89.1	165.4	3′ above split
	T1	....	21.0	....	...	Top of tube
B	S1	....	20.0	....	...	Split
	T1	17.4	51.7	146.3	167.7	Top of tube
C	S1	....	27.9	175.7	...	Split
	T1	....	41.9	132.4	...	Top of tube
D	S1	18.2	21.0	147.8	...	Split

Note: These values are averages of at least two values.

Fahr. (100 degrees Cent.) and again a sharp loss when tested at 32 degrees Fahr. (0 degrees Cent.).

4. Standard temper brittleness tests made on tube metal in all cases show the ratio of water-quenched specimens to those furnace cooled is greater than 2, which shows that the metal has a susceptibility to temper brittleness. This susceptibility ratio is lessened when the specimens are broken at 212 degrees Fahr. (100 degrees Cent.).

5. The effect of decrease of temperature on 4 to 6 per cent chromium steel is really twofold: first, it actually lowers the impact resistance of the steel; secondly, it increases the temper brittleness susceptibility of steel with the decrease of temperature.

Service Data on 4 to 6 Per Cent Chromium Plus Molybdenum Tubes

Quite recently, some data were obtained on tubes of 4 to 6 per cent chromium steel, also containing molybdenum, which were in service 4½ months. These were taken out of service due to the change of design in the heater. The physical properties of these tubes were determined before and after service and are included for comparison. The chemical analysis of the heat of steel from which tubes were made is as follows:

C	Mn	P	S	Si	Cr	Mo
0.14	0.45	0.015	0.015	0.34	5.27	0.48

The tubes were installed in heaters of different design so that they were in the heater in horizontal position. The service condi-

Table V
Temper Brittleness Tests Charpy Ft.-Lbs.

Tube Designation	Temperatures of Testing: 75° F. (25° C.) Quenched Specimens	75° F. (25° C.) Furnace Cooled Specimens	75° F. (25° C.) Ratio Q/F	212° F. (100° C.) Quenched Specimens	212° F. (100° C.) Furnace Cooled Specimens	212° F. (100° C.) Ratio Q/F
A	104.4	29.7	3.51	.....	.....	.....
B	109.9	37.8	2.90	111.9	90.8	1.23
C	122.3	45.8	2.67	124.5	118.3	1.05
D	143.4	62.0	2.30	144.1	140.3	1.025

Table VI
Effect of Service on Tensile Properties of Tube Metal of 4 to 6 Per Cent Chromium Steel Plus Molybdenum

Tube Designation	Section	Yield Strength Lbs./Sq. In. Original	Yield Strength Lbs./Sq. In. After Service	Tensile Strength Lbs./Sq. In. Original	Tensile Strength Lbs./Sq. In. After Service	Elongation in 2" Per Cent Original	Elongation in 2" Per Cent After Service	Reduction of Area Per Cent Original	Reduction of Area Per Cent After Service
E	Front	51600	41000	75900	71300	28	32.5	72.3	70.8
	Back[1]	49700	38800	76500	65500	30	35	73.7	74.2
F	Front	54400	43850	74800	73400	28	31	73.0	72.7
	Back	55500	36800	75700	68000	28	30	71.5	70.2
G	Front	46900	.....	74400	74700	31	31	68.4	71.8
	Back	40800	40500	74400	74700	30	32	75.1	65.2

Note—In these heaters the greatest heat density is toward the back end of the tubes.

Effect of Service on Impact Properties of 4 to 6 Per Cent Chromium Plus Molybdenum Tube Metal

Tube Designation	Front End: Charpy Ft.-Lbs. Izod Notch Original	Front End: Charpy Ft.-Lbs. Izod Notch After Service	Front End: Brinell Hardness Original	Front End: Brinell Hardness After Service	Back End: Charpy Ft.-Lbs. Izod Notch Original	Back End: Charpy Ft.-Lbs. Izod Notch After Service	Back End: Brinell Hardness Original	Back End: Brinell Hardness After Service
E	48.4	127.7	129	115	51.7	128.7	128	103
F	70.9	114.5	127	116	52.4	109.0	138	105
G	83.2	110.4	129	121	93.1	121.2	123	121

Note: All specimens were broken at about 85° F. (30° C.) and were notched with a "V" Izod Notch.

Variation of Impact Property with Temperature

Tube Designation	Charpy Ft.-Lbs.—Izod "V" Notch: −40° F. (−40° C.)	0° F. (−18° C.)	32° F. (0° C.)	85° F. (30° C.)	212° F. (100° C.)
E	29.4	59.4	105.9	127.7	138.9
F	....	43.0	59.7	114.5	130.9

tions of operation were similar to the tubes in the vertical heater. Tables VI and VII, inclusive, show the physical properties of these tubes.

These tables show that as a result of service, the following changes took place:

1. Strength of metal decreased while the ductility in-

creased, these changes being greater in portions of the tubes subject to greater heat.

2. The impact properties of the metal improved considerably. Evidently slow cooling of the tubes did not embrittle the metal as is commonly the case with plain 4 to 6 per cent chromium steels. The metal does not have any temper brittleness; neither does the metal lose its resistance to impact as rapidly at lower temperatures as the 4 to 6 per cent chromium steel.

Discussion of Service Data

Comparative impact properties of the two types of steels, 4 to 6 per cent chromium and 4 to 6 per cent chromium plus molybdenum, illustrate the different behavior of the two steels in service, as far as a tendency to cold embrittlement is concerned. While it is true that the installations of 4 to 6 per cent chromium-molybdenum tubes in the author's company plants have not been numerous, nor have they been in service as long as 4 to 6 per cent chromium tubes, no cold embrittlement failures of 4 to 6 per cent chromium-molybdenum tubes are known. H. D. Newell (4) reports no such failures in several thousands of tons of tubing of this analysis.

Particularly, these two types of steel vary in their response to laboratory temper brittleness test. It appears, however, that the time element is a very important factor in these failures. Statistical observation of thousands of tubes in service was made, and of approximately fifty such failures, nearly all occur when the tubes were in service two or three years. Slow cooling from the operating temperature of a brittle tube actually improved the impact properties. This was illustrated by the experiment on metal from tube H of plain 4 to 6 per cent chromium analysis, which failed due to cold splitting, and which is shown in Table VIII.

Table VII
Temper Brittleness Susceptibility

Tube Designation	Quenched Specimen		Furnace Cooled Specimen		
	Charpy Impact Values Ft.-Lbs.	Brinell Hardness	Charpy Impact Values Ft.-Lbs.	Brinell Hardness	Ratio
E at 79° F. (37° C.)	136.3	185	155.0	192	.88
E at 0° F. (—18° C.)	152.3		140.8		1.08
F at 79° F. (37° C.)	126.5	192	142.7	187	.87
F at 32° F. (0° C.)	131.9		140.2		.94

Note: These temperatures are those at which the specimens were broken.

Table VIII
Effect of Heat Treatment on Impact Resistance of Metal from Failed 4 to 6 Per Cent Chromium Tube

	Bottom Section of Tube		Middle Section of Tube	
	Charpy Ft.-Lbs. Izod Notch	Brinell Hardness	Charpy Ft.-Lbs. Izod Notch	Brinell Hardness
Properties after failure	65.1	138	14.8	114
Furnace Cooled from 1200° F. (650° C.)	140	140	92.7	110
Quenched in Water from 1200° F. (650° C.)	141.2	159	125	112

Note—The cooling rate of furnace from 1250 degrees Fahr. (675 degrees Cent.) is at the rate of 200 degrees during the next hour.

This time factor can also be shown by the comparative temper brittleness test and its modification. This is illustrated in Table IX. The steel was in bar stock form and was in the annealed condition. Its chemical analysis was as follows:

Carbon	Chromium	Silicon	Molybdenum
0.19	5.04	0.03	none

It would appear from this experiment that once the metal is annealed it will not matter how fast it is cooled. Actually, even though the tubes are installed in the annealed condition, they become embrittled after prolonged exposure to a range of temperature from 900 to 1200 degrees Fahr. (465 to 650 degrees Cent.).

Even though the laboratory temper brittleness test corresponded with the failures of tubing in service due to cold embrittlement, it was decided to make various standard stability and aging tests in order to

Table IX
Impact Resistance of 4 to 6 Per Cent Chromium Metal After a Standard and Modified Temper Brittleness Test

Quenched in Water from 1650° F. (900° C.)					Annealed at 1650° F. (900° C.)				
Quenched in H_2O from 1200° F. (650° C.)		Furnace Cooled from 1200° F. (650° C.)			Quenched in H_2O from 1200° F. (650° C.)		Furnace Cooled from 1200° F. (650° C.)		
Charpy Impact Values Ft.-Lbs.	Brinell Hardness	Charpy Impact Values Ft.-Lbs.	Brinell Hardness	Ratio	Charpy Impact Values Ft.-Lbs.	Brinell Hardness	Charpy Impact Values Ft.-Lbs.	Brinell Hardness	Ratio
162.3	192	38.1	197	4.26	197.6		213.9		
					222.6		207.7		
					223.6		212.5		
					224.7[1] Plus		224.7 Plus		Approx. 1

Note—Individual specimen values are given because some specimens had greater value than the capacity of the machine.

further correlate the laboratory tests with the actual behavior of steels in service, as well as to throw additional light upon the mechanism of the embrittlement.

Experiments

Since embrittlement of steels in service has some relation to the type of steel or to the particular heat involved, several different compositions were similarly tested. The chemical composition of experimental steels are shown in Table X. The various experiments are reported under the subheads.

Table X

Chemical Analysis of Steels Tested

Designation	Per Cent C	Cr	Si	Mo	Cu	Ti	Remarks
1. 4-6% Cr	0.15	5.04	0.18	....	....	....	
2. 4-6% Cr	0.12	5.08	0.30	....	....	....	
3. 4-6% Cr	0.11	5.11	0.49	....	....	....	
4. 4-6% Cr	0.125	5.32	0.30	....	....	....	
5. 4-6% Cr Mo	0.20	5.54	0.24	0.52	....	....	
6. 4-6% Cr Mo	0.07	5.57	0.26	0.44	....	....	
7. 4-6% Cr Cu	0.25	4.23	0.36	....	0.98	....	
8. 4-6% Cr Cu	0.255	4.45	0.56	....	1.01	....	
9. 4-6% Cr Ti	0.165	4.70	0.41	....	....	0.94	
10. C. S.	Mild Steel						

Stability Tests

Since the embrittlement in service results in a decrease of impact resistance in 4 to 6 per cent chromium steels, the variation of the properties of different steels can be experimentally checked by exposing the various specimens in actual refining units under various conditions of temperature. In these locations the specimens are likewise subjected to alternate heating and cooling cycles. Both plant and laboratory stability tests were made.

Test 1—Plant—In this test annealed specimens were exposed to temperatures of 700 degrees Fahr. (370 degrees Cent.) and 810 degrees Fahr. (430 degrees Cent.) for 3452 and 3147 hours, respectively, in the stills of the cracking units. The tensile and impact properties are shown in Table XI.

Test 2—Laboratory—In this test the stability of impact properties was determined by heating the specimens in the laboratory muffle-type electric furnace for 2 to 250 hours and determining the comparative properties. This test is similar to the one employed by

Table XI

Change in Tensile Properties After Exposure in Refining Units

Number and Type of Steel	Tensile Strength Lbs. Per Sq. In.			Elongation in 2" Per Cent			Reduction of Area Per Cent			Brinell Hardness		
	Original	700° F. (370° C.)	810° F. (430° C.)	Original	700° F. (370° C.)	810° F. (430° C.)	Original	700° F. (370° C.)	810° F. (430° C.)	Original	700° F. (370° C.)	810° F. (430° C.)
1. 4-6% Cr	58700	57850	59125	38	37.0	39.5	73.5	74	74	107	109	107
2. 4-6% Cr	87400	88500	86700[1]	26.5	26.0	25.5	80.8	79.1	79.2	179	183	183
3. 4-6% Cr	94800[1]	96600	97925[1]	25	25	25	75.6	76.6	73.0	207	201	207
4. 4-6% Cr	90200	90700	89500	25	26.5	25	77.4	82.1	77.1	183	187	183
5. 4-6% CrMo	64000	65100	64600	38.5	39	38	74.8	75.5	74.8	126	126	121
6. 4-6% CrMo	105000	105500	108500	22	21.5	21.5	74.0	74.1	73.2	229	229	235
7. 4-6% CrCu	.....	109000	99500	....	23.0	24.5	....	58.3	63.4	...	217	207
8. 4-6% CrCu	94200	109600	98000	26.5	24.5	25.0	66.6	65.7	64.6	183	217	201
9. 4-6% CrTi	63300	60300	64300	38.5	30.0	37.0	75.3	69.8	74.4	121	116	121
10. Carbon	52000	52000	52200	41.5	40	41.5	72.4	73.0	72.2	101	95	99

Note 1—Specimens defective either due to internal seams or rolling defects characterized either by longitudinal or transverse cracking or breaking.

Change in Impact Properties After Exposure in Refining Units

Number and Type of Steel	Alternate Charpy Specimens—V Notch Ft.-Lbs.			Brinell Hardness		
	Original	700° F. (370° C.)	810° F. (430° C.)	Original	700° F. (370° C.)	810° F. (430° C.)
1. 4-6% Cr	127.8	37.2*	54.7	101	101	101
2. 4-6% Cr	136.4*	16.1	11.3	178	178	178
3. 4-6% Cr	45.2	13.8	11.4	189	185	200
4. 4-6% Cr	165.6	61.8	35.0	178	171	178
5. 4-6% CrMo	165.5	156.7	149	114	114	114
6. 4-6% CrMo	156.3	145.8	142.4	216	200	218
7. 4-6% CrCu	16.1	8.3	7.8	165	200	178
8. 4-6% CrCu	142.2	8.5	10.1	143	200	178
9. 4-6% CrTi	58.7	14.8	56.1	114	112	119
10. Carbon	137.8	112.3*	140.0	95	90	90

Note 1—Values marked with (*) were very erratic but represent averages of at least four different specimens.

Bailey and Roberts (5). In order to check the influence of previous heat treatment, half of the specimens were annealed and half normalized from 1700 degrees Fahr. (925 degrees Cent.). The tempering treatment was 750 degrees Fahr. (400 degrees Cent.) and 850 degrees Fahr. (455 degrees Cent.)—the first temperature, 750 degrees Fahr. (400 degrees Cent.), might not have been exact, actual temperature being lower, since it was found, after the experiment, that the temperature controller was not registering the set temperature, due to the cells being weakened. The figures must be accepted with this reservation. The obtained data are shown in Table XII.

Aging Tests

Aging After Quenching—In this test, the capacity for age-

Table XII
Change in Impact Properties After Heating at 750 Degrees Fahr. (400 Degrees Cent.)

Number and Type of Steel	Annealed Specimens: Charpy Impact Values Ft.-Lbs. 2 Hrs.	Annealed Specimens: Charpy Impact Values Ft.-Lbs. 200 Hrs.	Annealed Specimens: Brinell Hardness 2 Hrs.	Annealed Specimens: Brinell Hardness 200 Hrs.	Normalized Specimens: Charpy Impact Values Ft.-Lbs. 2 Hrs.	Normalized Specimens: Charpy Impact Values Ft.-Lbs. 200 Hrs.	Normalized Specimens: Brinell Hardness 2 Hrs.	Normalized Specimens: Brinell Hardness 200 Hrs.
1. 4-6% Cr	155	165.9	101	101	38.4	31.4	341	352
2. 4-6% Cr	82.6*	56.8	121	119	52.7	26.0	383	392
3. 4-6% Cr	53.4	37.3	129	128	57.8	31.4	388	397
4. 4-6% Cr	40.0	29.7	124	122	51.5	25.3	406	415
5. 4-6% Cr Mo	132.9	60.2	116	126	39.9	25.1	363	384
6. 4-6% Cr Mo	159.4	157.7	115	116	42.7	29.4	363	380
7. 4-6% Cr Cu	26.3	22.2	171	200	40.6	23.8	477	477
8. 4-6% Cr Cu	25.3	21.7	171	200	34.1	28.6	444	472
9. 4-6% Cr Ti	65.8	83.7*	107	107	92.7	114.4	114	112
10. Carbon	30.1	31.0	84	83	....	151.0	...	89

(*) Erratic results average of three values.

Change in Impact Properties After Heating at 850 Degrees Fahr. (455 Degrees Cent.)

Number and Type of Steel	Annealed Specimens: Charpy Impact Values Ft.-Lbs. 2½ Hrs.	Annealed Specimens: Charpy Impact Values Ft.-Lbs. 250 Hrs.	Annealed Specimens: Brinell Hardness 2½ Hrs.	Annealed Specimens: Brinell Hardness 250 Hrs.	Normalized Specimens: Charpy Impact Values Ft.-Lbs. 2½ Hrs.	Normalized Specimens: Charpy Impact Values Ft.-Lbs. 250 Hrs.	Normalized Specimens: Brinell Hardness 2½ Hrs.	Normalized Specimens: Brinell Hardness 250 Hrs.
1. 4-6% Cr	144.2	97.8	97	100	20.8	23.3	334	207
2. 4-6% Cr	51.5	34.4	116	112	20.5	16.6	363	229
3. 4-6% Cr	40.0	21.8	117	116	17.3	17.6	375	225
4. 4-6% Cr	39.4	16.4	121	124	23.0	21.4	388	241
5. 4-6% Cr Mo	100	65.5	114	114	24.1	27.7	348	321
6. 4-6% Cr Mo	189	153.2	114	112	38.4	108.9	345	269
7. 4-6% Cr Cu	16.1	12.8	171	162	25.5	18.4	415	280
8. 4-6% Cr Cu	16.4	14.8	171	165	28.4	19.2	424	285
9. 4-6% Cr Ti	52.8	78.4	103	103	21.8	47.0	107	105
10. Carbon	23.5	20.8	83.4	91	139.3	110.2*	91	92

(*) Erratic results average of three values.

hardening of these steels after suitable heat treatment, namely; quenching from approximately above and below A_1 point was investigated. The tensile specimens were quenched from indicated temperatures and on half the number, the tensile properties were determined the same day; on the other half, these were determined after aging for 30 days at room temperature. The obtained results are shown in Table XIII.

In order to obtain a precipitation hardening on copper steels, it is necessary to reheat the supersaturated solutions of copper in iron. This has been shown by Lorig and MacLaren (6) with plain copper steels and by Bucholtz and Köster (6) with copper-chromium steels. They showed that reheating for four hours at 930 degrees Fahr. (500 degrees Cent.) was an effective treatment. The change in Brinell hardness after such treatment is shown in Table XIV.

Aging After Cold Work Deformation—In this test the steels were tested as follows:

The tensile tests were made $\frac{1}{16}$ inch oversize in diameter and elongated 10 per cent in a tensile machine. The specimens were then machined to 0.505 inch diameter, when one set of specimens was tested immediately after machining, and the other set after aging for 30 days at room temperature. The obtained results are shown in Table XV.

Steel No. 8, chromium-copper alloy, was also subjected to 10 per cent extension and then aged at elevated temperature. The steel did not age as is seen from the following results:

Steel No. 8	Yield Point Lbs. Per Square In.	Tensile Strength Lbs./Sq. In.	Elongation % in 2"	Reduction of Area
Cold-Worked	111,500	112,125	15.5	72.0
Cold-Worked and aged 3 hours at 930 degrees Fahr.	95,500	107,000	21.0	73.6

Table XIII

Change in Tensile Properties and Brinell Hardness Resulting from Artificial Aging

Number and Type of Steel	Tensile Strength Lbs. Per Sq. In. As Quenched	Tensile Strength Lbs. Per Sq. In. Aged	Elongation Per Cent in 2 Inches As Quenched	Elongation Per Cent in 2 Inches Aged	Reduction of Area Per Cent As Quenched	Reduction of Area Per Cent Aged	Brinell Hardness As Quenched	Brinell Hardness Aged
Quenching Temperature 1100 Degrees Fahr. (593 Degrees Cent.)								
1. 4-6% Cr	57500	58700	38	37.5	74	74.4	107	109
2. 4-6% Cr	86250	86900	26	25	79.5	77.9	187	192
3. 4-6% Cr	95000	95300	24	24	77.2	77.3	201	201
4. 4-6% Cr	89250	88200	27	26	77.4	78.0	187	192
5. 4-6% Cr Mo	64850	65000	38	37.5	78.9	75.0	126	121
6. 4-6% Cr Mo	105650	103500	21	20.5	75.2	73.8	229	229
8. 4-6% Cr Cu[1]							192	179
9. 4-6% Cr Ti	63100	63400	36	38	75.6	74.7	131	126
10. Carbon	53500	58000	38.5	32.5	73.0	70.5	111	111
Note 1—All specimens in Bar 8 were defective; poor forging.								
Quenching Temperature 1300 Degrees Fahr. (705 Degrees Cent.)								
1. 4-6% Cr	58400	58500	38	38	73.8	75.4	116	107
2. 4-6% Cr	88200	87500	26	25	80.0	80.4	187	187
3. 4-6% Cr	94650	93500	25	24	77.7	78.3	201	201
4. 4-6% Cr	88000	88750	26	26	77.5	78.1	192	183
5. 4-6% Cr Mo	66700	64400	37.5	38	78.6	75.9	128	126
6. 4-6% Cr Mo	84200	85000	27.5	25	78.4	78.0	187	183
8. 4-6% Cr Cu							170	170
9. 4-6% Cr Ti	64800	62400	37.5	35	79.7	74.2	121	114
10. Carbon	63000	87000	34.5	23	70.0	58.7	128	179
Quenching Temperature 1500 Degrees Fahr. (815 Degrees Cent.)								
1. 4-6% Cr	61900	59700	30	32	73.3	73.9	170	140
2. 4-6% Cr	151200	150000	13.5	10.5	50.1	48.5	352	363
3. 4-6% Cr	105250	95400	15.0	16.5	62.4	70.8	183	187
4. 4-6% Cr	165500	137800	7.5	8.0	47.9	44.9	277	187
5. 4-6% Cr Mo	68100	72600	32.5	18.0	72.9	72.0	126	134
6. 4-6% Cr Mo	89700	76100	31.0	24.5	70.7	79.0	156	152
8. 4-6% Cr Cu							444	444
9. 4-6% Cr Ti	61000	61750	35.0	24.0	74.3	75.2	118	128
10. Carbon	62900	81900	33.0	24.0	69.4	61.7	131	170

Table XIV

Brinell Hardness Values After Artificial Aging of 4 to 6 Per Cent Chromium Steels[1]

Number and Type of Steel	Quenching Temperature 1300°F. (705°C.) As Quenched	Aged 4 Hrs. 212°F. (100 °C.)	As Quenched	Aged 4 Hrs. 930°F. (500 °C.)	Quenching Temperature 1500°F. (815°C.) As Quenched	Aged 4 Hrs. 212°F. (100 °C.)	As Quenched	Aged 4 Hrs. 930°F. (500 °C.)
1. 4-6% Cr	121[2]	116	121	111	311	302	311	285
2. 4-6% Cr	187	183	187	179	363	363	363	302
3. 4-6% Cr	187	207	187	201	382	362	363	321
4. 4-6% Cr	201	187	187	179	388	388	388	341
5. 4-6% Cr Mo	126	126	126	126	352	341	341	321
6. 4-6% Cr Mo	174	170	174	174	311	311	311	302
7. 4-6% Cr Cu	179	170	179	187	461	444	444	341
8. 4-6% Cr Cu	174	170	174	187	444	444	444	341
9. 4-6% Cr Ti	121	121	124	116	121	121	122	121
10. Carbon	114[3]	129	121	95	119	121	121	101

Note 1—Specimens were held one hour at temperature before quenching.

Note 2—Specimens were taken about ½ inch long polished on both ends. One end was read after quenching and other end after aging.

No. 3—Brinell hardness of carbon steel specimens was determined under 1000 kilo load.

Table XV

Comparative Tensile Properties of Steels on Aging After Cold Work Deformation

Number and Type of Steel	Yield Strength Lbs. Per Sq. In. Original	After 10 Per Cent Elongation	After 10 Per Cent Elongation and Aging	Tensile Strength Lbs. Per Sq. In. Original	After 10 Per Cent Elongation	After 10 Per Cent Elongation and Aging	Per Cent Increase in Tensile Properties on Aging
1. 4-6% Cr	27400	50050	60000	58700	62600	65000	4.0
2. 4-6% Cr	73700	92500	94000	87400	93700	96600	3.1
3. 4-6% Cr	82400	99700	103600	94800	103000	103600	0.6
4. 4-6% Cr	74200	93000	96650	90200	93900	97900	4.25
5. 4-6% Cr Mo	30750	57750	69150	64000	69500	72000	3.6
6. 4-6% Cr Mo	93000	115250	115700	105000	115250	115700	.4
7. 4-6% Cr Cu	.....	107500	121250	.....	116000	123100	6.1
8. 4-6% Cr Cu	62000	98350	110400	98000	105000	111750	6.4
9. 4-6% Cr Ti	29400	56750	68500	63300	68000	71350	4.9
10. Carbon	39200	45350	62750	52000	55350	67750	18.3

	Elongation in 2 Inches			Reduction of Area			Decrease in Elongation
1. 4-6% Cr	38	32.5	29	73.5	72.1	72	10.8
2. 4-6% Cr	26.5	21	18.5	80.8	78.4	77.3	11.9
3. 4-6% Cr	25	20	17.5	75.6	74.2	73.8	12.5
4. 4-6% Cr	25	22	17.5	77.4	77.3	75.4	20.4
5. 4-6% Cr Mo	38.5	32.5	28.5	74.8	73.0	72.3	12.3
6. 4-6% Cr Mo	22.0	16.5	15	74.0	72.1	72.2	.9
7. 4-6% Cr Cu	....	18	13	....	55.8	51.5	27.5
8. 4-6% Cr Cu	25	21	16	64.6	61.5	58.7	23.8
9. 4-6% Cr Ti	38.5	32	28	75.3	73.4	70.6	12.5
10. Carbon	41.5	33	20	72.4	69.8	64.5	39.4

Temper Brittleness Tests

Temper brittleness tests on these steels were made exactly as described in the earlier part of the paper. The results obtained are shown in Table XVI.

Table XVI

Temper Brittleness Test

Number and Type of Steel	32°F. (0°C.)			89°F. (32°C.)				212°F. (100°C.)		
	Quenched Specimen Charpy Impact Values Ft.-Lbs.	Furnace Cooled Specimen Charpy Impact Values Ft.-Lbs.	Ratio	Quenched Specimen Charpy Impact Values Ft.-Lbs.	Quenched Specimen Brinell Hardness	Furnace Cooled Specimen Charpy Impact Values Ft.-Lbs.	Furnace Cooled Specimen Brinell Hardness	Ratio	Quenched Specimen Charpy Impact Values Ft.-Lbs.	Furnace Cooled Specimen Charpy Impact Values Ft.-Lbs.	Ratio
1. 4-6% Cr	146.1	63.9	2.28	141.3	169	139.8	174	1.01	136.9	133.9	1.02
2. 4-6% Cr	176.1	20.6	8.54	192	187	103.5	179	1.86	179	176.8	1.01
3. 4-6% Cr	166.9	19.0	8.8	174	197	22.1	...	7.90	172.8	161.6	1.08
4. 4-6% Cr	159.5	45.0	3.54	155.6	197	66.6	187	2.39	162.3	156.9	1.02
5. 4-6% Cr Mo	94.8	98.4	.97	95.4	207	95.4	202	1.00	.....	.....	....
6. 4-6% Cr Mo	170.7	172.8	.99	171	179	172.8	183	.99	.....	.....	....
8. 4-6% Cr Cu	52.3	28.7	1.82	89.7	229	27.0	229	3.3	.....	.....	....
9. 4-6% Cr Ti	56.6	29.7	1.90	126.6*	114	81.2*	114	1.56	186.4	127	1.46
10. Carbon	144.6	160.4	.90	128.0	129	160.5	95	.80	.....	.....	....

*Results erratic; individual quenched specimens were 149.4; 162.3; 18.8; 104.8; 89.8. Individual furnace cooled specimens were 80.8; 17.0; 89.8; 20.1; 73.1.

The Effect of Low Temperatures on Impact Properties

Since studies of impact of metal from failed tubes revealed it to be extremely sensitive to the effect of temperature, several of these steels were tested for impact at low temperatures. The obtained results are shown in Table XVII.

Table XVII

The Effect of Low Temperatures on Impact Properties of Steel of 4 to 6 Per Cent Chromium Type

Number and Type of Steel	Charpy Impact Values Ft.-Lbs. at Designated Temperatures 72°F. (22°C.)	52°F. (10°C.)	28°F. (−2°C.)	0°F. (−18°C.)	−40°F. (−40°C.)
2. 4-6% Cr		97.8	14.6	13.4	17.6
2. 4-6% Cr		18.2	18.8	18.2	13.4
2. 4-6% Cr		20.1	32.9	18.8	13.4
Average	136.4	45.4	22.1	16.8	14.8
4. 4-6% Cr		146.6	71.1	22.1	16.3
4. 4-6% Cr		66.4	58.1	18.8	16.3
4. 4-6% Cr		157.8	42.4	14.0	22.1
Average	165.6	123.6	57.2	18.3	18.2
5. 4-6% Cr Mo		172.0	173.6	98.8	149.4
5. 4-6% Cr Mo		164.0	161.4	134.9	146.6
5. 4-6% Cr Mo		161.4	157.8	156.0	149.4
Average	165.5	165.8	164.3	129.9	148.5
9. 4-6% Cr Ti		31.4	40.8	9.6	10.6
9. 4-6% Cr Ti		63.6	31.4	18.2	9.6
9. 4-6% Cr Ti		12.8	10.1	10.6	11.2
Average	58.7	35.9	27.4	12.8	10.4

NOTE—Since the results obtained were very erratic all of the values are presented. The average results are also given in order to bring out more clearly the effect of temperature on the impact property even though it is admitted that, statistically, these averages are not correct.

DISCUSSION OF EXPERIMENTAL TESTS

Stability

Plant Tests—The tensile properties, after exposure to 700 degrees Fahr. (370 degrees Cent.) and 810 degrees Fahr. (430 degrees Cent.) for some three thousand hours, did not show much variation previous and after exposure. Steels Nos. 7 and 8, chromium-copper, showed some increase in tensile strength and Brinell hardness after exposure to 750 degrees Fahr. (400 degrees Cent.). The impact values of plain 4 to 6 per cent chromium steel drop significantly, practically paralleling the service tests. This is also true of chromium steels alloyed, in addition, with copper and titanium, while molybdenum steel showed practically no change.

Laboratory Tests—In considering annealed specimens, one can readily see that the obtained data did not show any significant trend. Chromium-copper steels showed some increase in hardness when exposed to 750 degrees Fahr. (400 degrees Cent.) and chromium-titanium steels were the only ones which showed improvements in properties after prolonged tempering. No difference in behavior is noticed between 4 to 6 per cent chromium steels and those alloyed with molybdenum. The normalized specimens did not reveal any significant results. There is some increase in hardness in specimens heated for 200 hours at 750 degrees Fahr. (400 degrees Cent.) compared with large drop of hardness in the specimens heated at 850 degrees Fahr. (445 degrees Cent.).

Generally, it appears that this test does not appear to correlate with service data as well as the plant test. The data do not show as significant trend in the laboratory test as in the plant test. The same is true, in our opinion, of data presented by Bailey and Roberts (5), in their Table I.

Aging

Aging After Quenching—(a) Tensile properties; no significant changes in these when steels were quenched from 1100 degrees Fahr. (595 degrees Cent.); when quenched from 1300 degrees Fahr. (705 degrees Cent.) and 1500 degrees Fahr. (815 degrees Cent.), carbon steel aged considerably while the 4 to 6 per cent chromium type steels showed practically no change.

(b) None of the steels were aged to any significant extent when held at elevated temperatures, judging from Brinell hardness values. This test does not appear to parallel the service behavior of tube metals.

Aging After Cold Work Deformation—The results obtained in this test follow closely results obtained on aging after quenching; 4 to 6 per cent chromium steels had only a nominal increase in strength due to aging, while the carbon steel increased 18.3 per cent.

Temper Brittleness Tests

Experimental temper brittleness tests, as well as those made on tube metal, checked with the service failures. At 32 degrees Fahr. (0 degree Cent.), all 4 to 6 per cent chromium steels, outside of those alloyed with molybdenum, showed susceptibility to temper brit-

tleness. At 89 degrees Fahr. (32 degrees Cent.), only one heat of 4 to 6 per cent chromium steel, not containing molybdenum, did not show tendency toward temper brittleness. This relationship can be brought out more forcibly, as follows:

1. Carbon steel is not temper brittle—no cases of cold splits.
2. 4 to 6 per cent chromium steel is temper brittle—several cases of cold splits occurred.
3. 4 to 6 per cent chromium steel, alloyed with molybdenum, is not temper brittle—no known cases of cold split tubes.

(This is further emphasized with 4 to 6 per cent chromium steels, alloyed with tungsten, which were found temper brittle in all cases examined by us. Cases of cold splits of this analysis, in service, have occurred.)

The Effect of Low Temperatures on Impact Properties

The impact properties, as with most steels, show considerable decrease in resistance to impact with the decrease of temperature. The particular heat of 4 to 6 per cent chromium, alloyed with molybdenum, shown in Table XVII, is probably better than the average; still, this steel appears to be in a class by itself, when compared with plain chromium steel or that alloyed with titanium.

Mechanism of Embrittlement

While this embrittlement, resulting in failures, is of great practical importance to the oil refinery engineer, it is also of great interest to the metallurgist who has to eliminate these failures through the study of the cause of this embrittlement.

These failures, as brought out in this paper, directly correlate with the laboratory temper brittleness test, which is an artificial test recommended by Rogers (7), Greaves (3), Jones (3), and other English investigators to evaluate the degree of susceptibilty to brittleness of steel on tempering.

The time factor, in influencing the temper brittleness results, has been recognized as important by practically every investigator of this phenomenon. Practical statistical observations of these

failures also confirmed the significance of time of service in bringing about this embrittlement. Many considerations lead one to speculate whether this type of phenomena may not be related to aging phenomena. The thought that temper brittleness may also be a type of aging has been also entertained by Merica (8) and French (9). The cause for temper brittleness has been thought to be due to separation of carbides from solution on slow cooling. Aging, after overstrain, and blue brittleness are thought to be also the result of dispersion hardening by many investigators. While there is no doubt that the age hardening of many systems of alloys, such as duralumin, at the elevated temperature, is due to dispersion hardening, the evidence that temper brittleness in general, and the embrittlement of 4 to 6 per cent chromium steels in particular, is due to the same cause, is very indirect and is, in our opinion, incompatible with some facts such as were observed during the course of the study of this embrittlement.

Different Causes for Temper Brittleness and Aging

Embrittlement or appreciable hardening of 4 to 6 per cent chromium steel could not be brought about experimentally by aging either after quenching or after strain deformation under conditions which aged the carbon steel. Remembering that carbon steel is not temper brittle, and 4 to 6 per cent chromium steel is, it would appear from these experiments that temper brittleness is not caused by the same phenomena that cause the aging of carbon steel.

Reversibility of the Embrittlement

Aging of steel is an irreversible process; accompanying embrittlement and hardening can only be removed by resolution of the precipitated constituent; embrittlement caused by the temper brittleness process is only temporary as, for example, can be seen from values shown in Table VI, and also in Table XVIII. In the latter table, specimens tested at 77 degrees Fahr. (25 degrees Cent.) had a low value, specimens from the same sections had high values at 212 degress Fahr. (100 degrees Cent.), and similar specimens, when cooled to room temperature, had, again, the same value as if they never had been heated to 212 degrees Fahr. (100 degrees Cent.). Variation of a few degrees in temperature results in greater than

Table XVIII

Influence of Small Changes in Temperature on Impact Properties of 4 to 6 Per Cent Chromium Steel[1]

Specimen Number	Charpy Impact Values Ft.-Lbs. at Designated Temperature 32°F. (0°C.)	77°F. (25°C.)	212°F. (100°C.)
43 B[2]	....	12.5	88.8
43 S	....	10.8	82.8
43 T	....	86.3	151.8
Specimens Heated at 212°F. (100°C.) and then Broken			
43 B	11.7	11.7	....
43 S	10.2	10.9	....

Note 1—The tested steel was from a tube which cracked half-way up in the furnace as a result of embrittlement. Its ratio of temper brittleness susceptibility was 3.67 at 77 degrees Fahr. (25 degrees Cent.) and 2.49 at 212 degrees Fahr. (100 degrees Cent.).

Note 2—Specimens 43 B were taken from the bottom of the tube, 43 S from the split section and 43 T from the top of the tube. Each value in the tubes is an average of at least two figures.

100 per cent change in impact properties. It appears improbable that such wide variation in properties in the narrow range of temperatures is due to any physical change in metal structure, such as precipitation or re-solution of some constituent when these occur at ordinary temperatures.

The reversibility of this phenomenon is similar to the effects of low temperatures on metals which W. J. DeHaas and Robert Hadfield (10) report to be temporary, that is, generally when metals are subjected to low temperatures, on return to ordinary temperatures, these metals are no better or worse for their having been subjected to cold. This temporary brittleness, in their opinion, involves no change in structure. Similarly, K. Heindlhofer (11), referring to abrupt change in apparent plasticity of iron, as shown by the impact test, at a critical temperature of —4 degrees Fahr. (—20 degrees Cent.) to —22 degrees Fahr. (—30 degrees Cent.) says:

> "But the hypothesis of precipitation is untenable because the process of re-solution of the precipitated phase could not possibly go on rapidly enough at these temperatures to enable the material to regain its original plasticity as soon as it is warmed above the apparent brittle range."

Microscopic Examination for Intercrystalline Precipitation and Its Significance

Microscopic examination of the brittle and tough sections of the

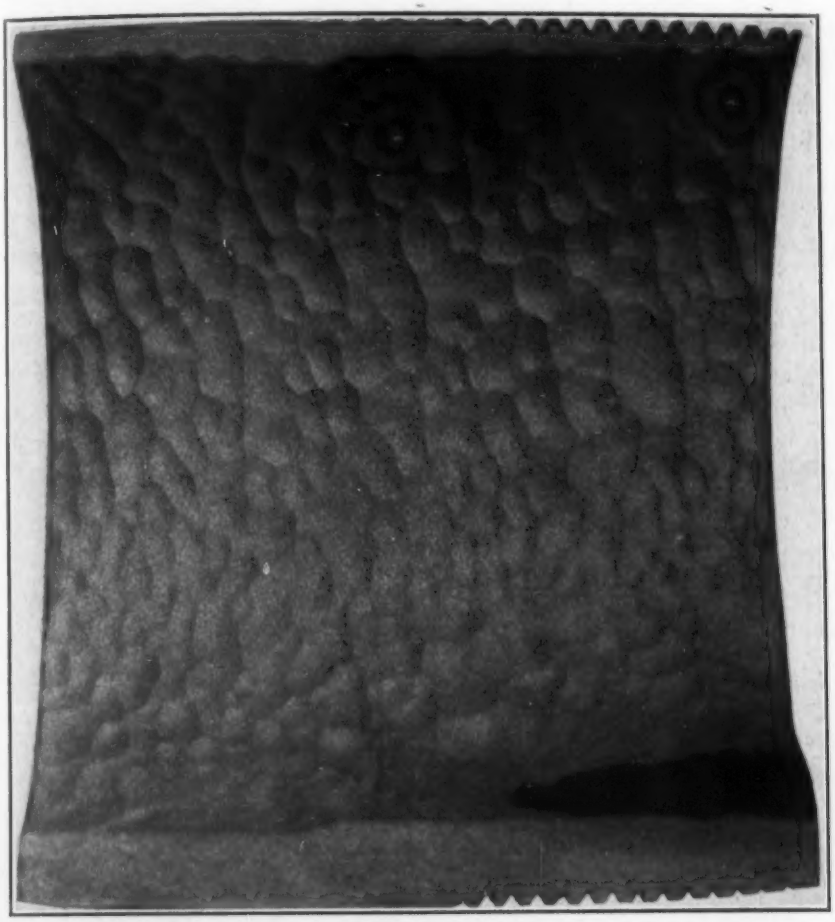


Fig. 3—Inside Surface of Corroded 4 to 6 Per Cent Chromium Steel Tube Which Shows Pitting Commonly Occurring in Tubes of the Plain Carbon Steel Class.

same tubes does not show any discernible difference in structure. A typical microstructure is shown in Fig. 4. It is to be noted that pearlite is still present in some grains; in the others the pearlite is all broken up into carbides and ferrite. The carbides precipitated in the grains proper.

Microscopic examination of 4 to 6 per cent chromium tubes which failed by cracking at ordinary temperature also show these to be intercrystalline. A metallurgist is apt to view with suspicion an intercrystalline fracture which occurs below equi-cohesive temperature of the metal. Embrittlement in boiler plate, caused by the combined action of stress and chemical attack when it results in fracture, takes place in an intercrystalline manner. This process of embrittlement is a part of aging phenomenon initiated by cold work

deformation and subsequent heating. The evidence that this type of cracking is preceded by intercrystalline precipitation is lacking, in this case, the same as in 4 to 6 per cent chromium steel.

The significance of intercrystalline cracking has lost some ground recently when Sauerwald, Schmidt and Kraemer (13) showed, in their study of brittleness of iron at low temperatures, that the fracture of brittle iron is usually transcrystalline, and only within a very

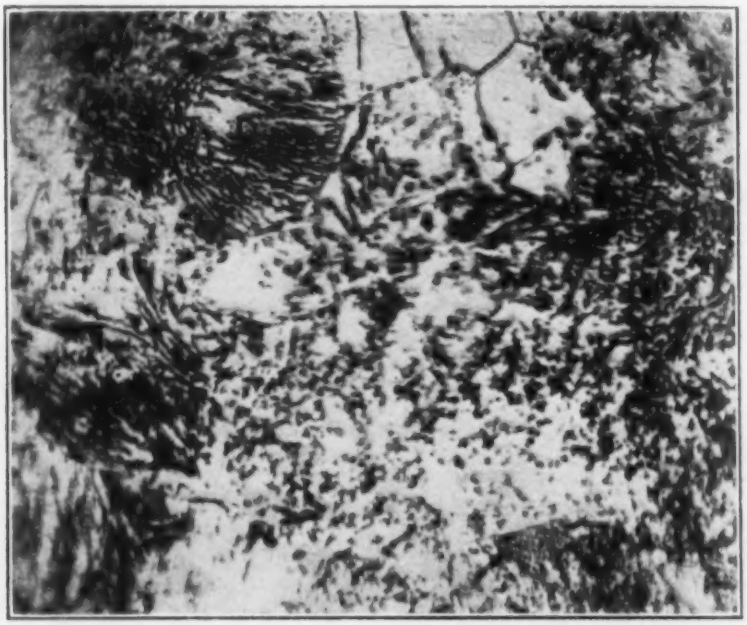


Fig. 4—Photomicrograph Showing Structure of 4 to 6 Per Cent Chromium Steel Taken from a Tube which Failed from Brittle Cracking after 29 Months Service. Etched in 5 Per Cent Nital. × 1000.

narrow range (—247 to —229 degrees Fahr.) (— 154 to —144 degrees Cent.) that the fracture may follow the grain boundary. They also state that the type of fracture depends on the orientation of the acting force with respect to the crystal. Thus the intercrystalline brittleness in iron alloys may not have any relation to intercrystalline precipitation.

Intercrystalline Precipitation and Corrosion

Intercrystalline precipitation in duralumin leads to intergranular corrosion. Due to intercrystalline precipitation of chromium carbides in 18 per cent chromium and 8 per cent nickel steel, chemical attack takes place also, preferentially, along grain boundaries. Thus, in many cases, the intercrystalline precipitation may be the cause of

intergranular chemical attack. In the refinery use, the 4 to 6 per cent chromium steel is not subject to intergranular corrosion either at high temperatures, when it is subjected to sulphide corrosion, or at comparatively low temperatures when it is subjected to water or steam corrosion. Fig. 3 illustrates an extreme case of corrosion. This tube was used as a part of a coil in heater service and after it corroded to minimum thickness specified for this service, it was used as a discharge line from an acid agitator neutralizing pump.

Although it is very desirable to know the cause of embrittlement of temper brittle steels, and a theory explaining temper brittleness may be very useful, the statements and data available which explain the above phenomenon are of such qualitative nature, and at times are so contradictory, that one must be very cautious in accepting theories that are not based on authentic service behavior of metals. The above discussion has been given with a view of emphasizing the caution necessary in accepting theories based on only indirect evidence when they attempt to explain the contradictory behavior of temper brittle steels.

Conclusion

A study of embrittled 4 to 6 per cent chromium tubes show that:

1. The tensile properties are uniformly good, comparatively as good as in original tubes prior to service.
2. The impact properties of embrittled sections decreased 80 per cent as compared to the average original tubes prior to service.
3. The impact properties show a precipitate rise when tested at 212 degrees Fahr. (100 degrees Cent.), and again a precipitate loss when tested at 32 degrees Fahr. (0 degree Cent.).
4. The metal has a high susceptibility to temper brittleness. This susceptibility rate is lessened when the specimens are broken at 212 degrees Fahr. (100 degrees Cent.).
5. The effect of decrease in temperature is twofold: first, it decreases the impact value of steel; secondly, it increases the susceptibility to temper brittleness.

A study of 4 to 6 per cent chromium tubes alloyed with molybdenum showed:

1. The impact properties suffer no deterioration as shown in this paper, or only very little deterioration as obtained elsewhere.
2. The metal does not show any susceptibility to temper brittleness.

Correlation between temper brittleness test and service embrittlement failures can be shown as follows:

1. Carbon steel tubes are not temper brittle—no brittle failures in service.
2. 4 to 6 per cent chromium steel tubes are temper brittle—brittle failures occurred.
3. 4 to 6 per cent chromium steel tubes alloyed with tungsten are temper brittle—brittle failures occurred.
4. 4 to 6 per cent chromium steel tubes alloyed with molybdenum are not temper brittle—brittle failures in service are not known.

Laboratory tests to determine the type of embrittlement showed 4 to 6 per cent chromium steel to be:

1. Not subject to experimental aging tests either after quenching from A_1 point or after strain hardening.
2. Subject to temper brittleness to a varying degree.
3. Very sensitive in impact value to the variation of temperature.

Both the experimental tests and service records fully agree with the brittle service failure. The practical value of this correlation lies in the fact that from the simple temper brittleness test the likelihood of the metal to suffer brittle failures in refinery use can be predicted.

Study of mechanism of embrittlement indicates that temper brittleness of metals is similar to brittleness suffered by iron alloys when these are subjected to low temperatures. The general theory that this phenomenon is related to precipitation of some constituent, commonly supposed to be carbide, is contradictory to several facts presented in this paper.

References

1. H. W. Gillett, "Notched Bar Tests," Editorial, *Metals and Alloys,* November 1931.

2. H. M. Wilten and E. S. Dixon, "Aging Embrittlement of 4 to 6 Per Cent Chromium Steels," *Proceedings,* American Society for Testing Materials, Vol. 34, Part II, 1934.
3. R. H. Greaves and J. J. A. Jones, "Temper Brittleness of Ni-Cr Steels," *Journal,* Iron and Steel Institute, Vol. CII, No. II, 1920.
4. H. D. Newell, Chief Metallurgist, The Babcock and Wilcox Tube Company, private communication, December 4, 1934.
5. R. W. Bailey and A. M. Roberts, "Testing of Materials for Service in High Temperature Steam Plant," *Engineering,* February 26, 1932.
6. J. L. Gregg and B. N. Daniloff, "The Alloys of Iron and Copper," McGraw-Hill Book Co., p. 152.
7. Rogers, *Journal,* Iron and Steel Institute, 1919, No. 2, p. 325.
8. P. D. Merica, "The Age Hardening of Metals," *Transactions,* American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, Vol. 99, 1932, p. 47.
9. H. J. French, "Fatigue and the Hardening of Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 21, October 1933, p. 919.
10. Prof. W. J. DeHaas and Sir Robert Hadfield, "On the Effect of the Temperature of Liquid Hydrogen on Tensile Properties of Metals," *Philosophical Transactions,* Royal Society, (1933), A715.
11. K. Heindlhofer, "The Plasticity of Iron at Low Temperatures," Technical Publication No. 581, Iron and Steel Division, American Institute of Mining and Metallurgical Engineers.
12. P. W. Bridgman, "The Physics of High Pressures."
13. F. Sauerwald, B. Schmidt and G. Kraemer, "The Brittleness Range of Iron at Low Temperatures," *Ztschr. f. Physik,* 67, p. 179-183, 1931.
14. E. Houdremont and H. Schrader, "The Question of Temper Brittleness," *Archiv für das Eisenhüttenwesen,* July, 1933, (49-59).
15. H. W. McQuaid, "Aluminum Additions in Modern Commercial Steels," *Metal Progress,* Nov., 1935, page 34.

DISCUSSION

Written Discussion: By H. D. Newell, chief metallurgist, The Babcock and Wilcox Tube Company, Beaver Falls, Pa.

Mr. Wilten presents a large amount of interesting data correlating the notch impact test with embrittlement failures in 4 to 6 per cent chromium steel cracking still tubes. The information given should be of interest to oil refinery engineers and other users of high temperature materials as well as to the metallurgical profession at large.

The writer has placed considerable reliance in the susceptibility test for indicating the tendency of pearlitic alloy steels to develop brittleness especially after failing to get any indication of such action by means of static tensile tests and hardness changes on aging at various temperatures. The "V" notch appears to detect greater differences in impact as a result of embrittlement than does the key-hole type notch. This is of interest as past attempts of the writer to correlate impact value with brittleness of tubes were so inconsistent that the writer finally adopted a ring flattening test to detect brittleness in tubes in preference to the impact test. The ring test consisted of simply cutting off sections of embrittled tubing and flattening under a power hammer after cooling or heating to various temperatures. The efficacy of the ring test in denoting

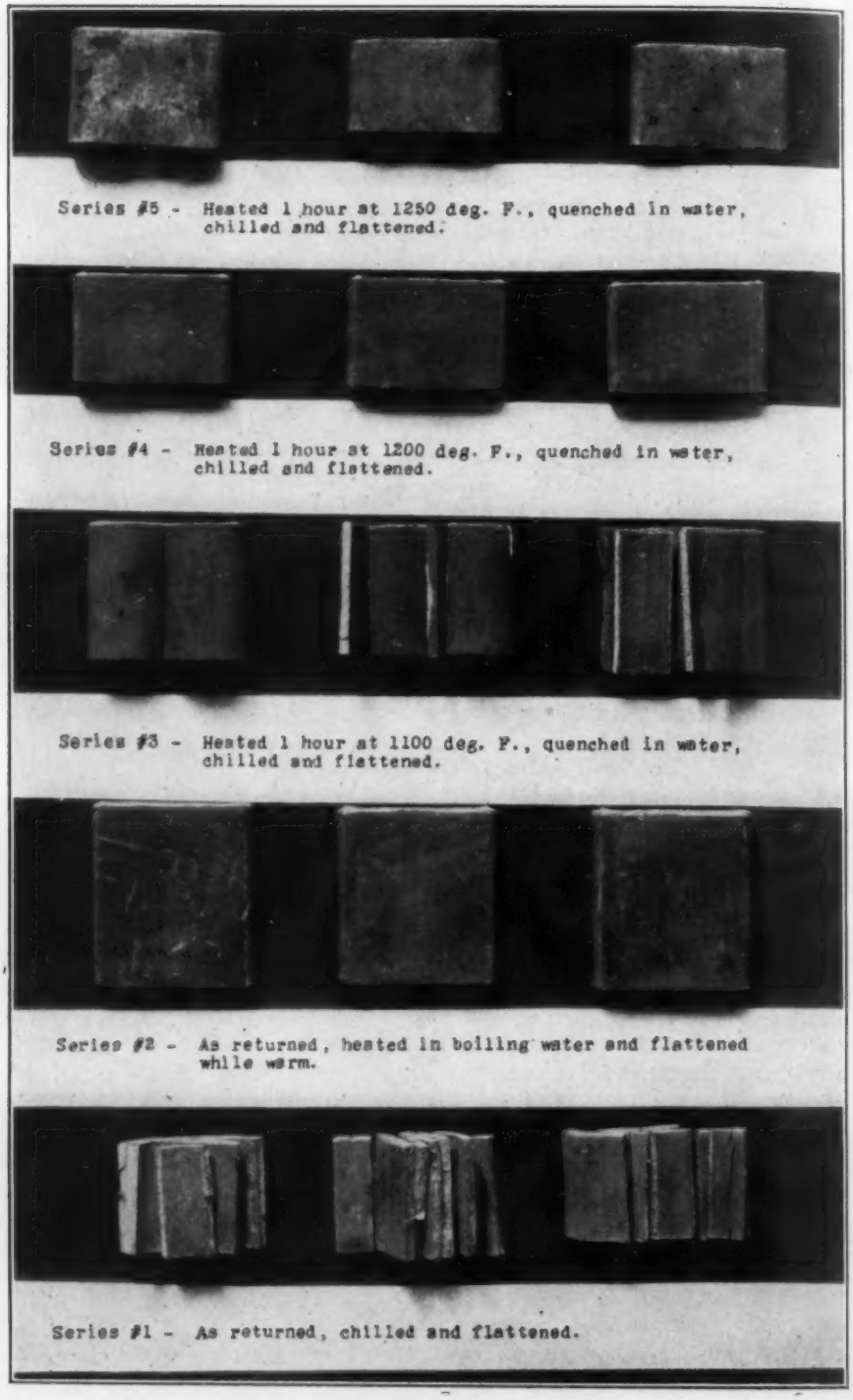

Series #5 - Heated 1 hour at 1250 deg. F., quenched in water, chilled and flattened.
Series #4 - Heated 1 hour at 1200 deg. F., quenched in water, chilled and flattened.
Series #3 - Heated 1 hour at 1100 deg. F., quenched in water, chilled and flattened.
Series #2 - As returned, heated in boiling water and flattened while warm.
Series #1 - As returned, chilled and flattened.

Fig. 1—Photographs Showing the Efficacy of the Ring Test in Denoting Brittleness.

brittleness may be noted in Fig. 1 of this discussion. While in effect, the ring test was simply a rather crude unnotched impact test, it proved very effective in detecting brittleness and in determining temperatures required to dissipate brittle tendencies. The ring test had the advantage that it tested the transverse properties of the tube whereas it is not practical to secure standard transverse Charpy specimens without flattening the tube section which is undesirable. Further, such a test can be used on small diameter thin walled tubes.

The influence of temperature on impact value and susceptibility is well demonstrated by Mr. Wilten and explains the practical observation that most tube embrittlement failures occur during winter months and were particularly distressing to Northern refineries. Embrittlement failures are definitely intercrystalline as may be noted in the accompanying photomicrographs (Fig. 2)

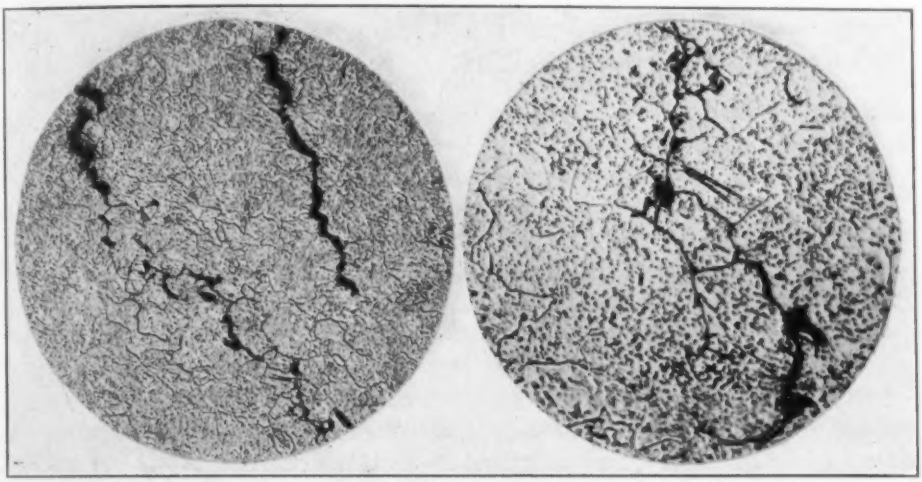


Fig. 2—Microstructure Near Terminal End of Cracks in Brittle 4-6 Per Cent Chromium Steel Cracking Still Tubes—After Service, Showing Intercrystalline Character of Cracks. Etch: Nital (Left) × 175. (Right) × 500.

of two different brittle tubes. This suggests some form of precipitation which interferes with mobility at grain boundary regions under conditions of rapidly applied stress. The mechanism of temper embrittlement is still somewhat obscure; however, it is held by the writer to be due to grain-boundary precipitation, possibly submicroscopic in size, as no appreciable differences in structure or hardness can be observed between the brittle and tough conditions.

The brittleness is transitory and may be alleviated under certain temperature environments such as warming to 212 degrees Fahr., or by quickly cooling from a temperature of about 1200 degrees Fahr (650 degrees Cent.). In the first case, the brittleness is not removed but is simply dissipated by warming and will return on cooling, while quenching from the higher temperature completely removes brittleness even when returned to low temperatures. Brittleness will then develop on further heating or slowly cooling through the "temper embrittlement" range which may be placed between 1100 and 700 degrees Fahr. (595 and 370 degrees Cent.).

Mr. Wilten's observations as to the time required to develop brittleness

do not altogether coincide with the writer's experiences. In the manufacture of tubing, several cases have developed wherein brittleness has occurred simply from too slow a cooling rate below 1100 degrees Fahr. (595 degrees Cent.), in the annealing operation. This has been particularly true of the tungsten type 4 to 6 per cent chromium alloy and suggests that tungsten makes the alloy even more susceptible toward development of brittleness. Plain 4 to 6 per cent chromium steel has been affected in a similar manner in annealing. In actual service, brittleness has been detected in tubes with only 400 hours service although many brittle tubes have operated over appreciable time periods before breakage has occurred.

Grain-size has an important part in development of temper brittleness and material which has been subjected to an artificial grain enlarging heat treatment is particularly disposed toward its development. In fact, the molybdenum containing alloy may become temper brittle if placed in large-grained condition. This suggests that grain-boundary extent and precipitation are intimately connected with temper brittleness of the type found in annealed 4 to 6 per cent chromium steel. The large-grained metal has a limited grain boundary extent and requires but slight precipitation to induce brittleness whereas fine-grained metal, due to a large amount of grain boundary extent, requires considerable precipitation, hence greater time at precipitation temperature is necessary before brittleness is induced. This would conform in general with the findings of Mr. Wilten's aging tests after heating at 750 and 850 degrees Fahr. (400 and 455 degrees Cent.). Molybdenum is probably effective in suppressing brittleness by reason of its grain refining action and because of its effect on the solubility of carbon in alpha iron.

The writer was particularly gratified at Mr. Wilten's conclusions that the impact value of 4 to 6 per cent chromium steel containing molybdenum does not suffer deterioration in impact value and that it does not show any susceptibility to temper brittleness. The first set of 4 to 6 per cent chromium-molybdenum tubes used in the American refining industry were installed at suggestions and specifications originating with the writer following an extended study of brittleness in plain 4 to 6 per cent chromium tubes. This was during the early part of 1931. The efficacy of molybdenum in suppressing cold brittleness has been well proven under practical operation and no cases of embrittlement have occurred in over four years service under all kinds of operating conditions with thousands of tubes in service. The improved creep strength of the molybdenum-containing alloy is so well known that it requires no comment. These features of improved strength and freedom from embrittlement have made the 4 to 6 per cent chromium-molybdenum alloy the preferred type for elevated temperature service and the plain and tungsten types are now more or less obsolete.

Mr. Wilten is to be congratulated on the extended study he has made on the impact and other properties of 4 to 6 per cent chromium steels.

Written Discussion: By Vincent T. Malcolm, director of research, and Thomas P. Jones, metallurgist, of the Chapman Valve Manufacturing Co., Indian Orchard, Mass.

We have read with considerable interest this paper by Mr. H. M. Wilten and are somewhat disturbed over the unfortunate use of the term, "embrittle-

ment," as there is no evidence presented that true embrittlement, such as shattering, is responsible for any of the phenomena discovered. It is true, there may be a loss of ductility or toughness due to one of several reasons other than brittleness. The use of the term, "embrittlement," is unfortunate also for another reason, as it tends to give one the impression that this type of failure differs radically from other types of failure under combined stress and temperature.

We believe that a more suitable term should be used in discussing this type of test as it is merely one phase of a large subject bearing on the influence of time, stress, and temperature.

In the light of the present information and knowledge, surprise may be felt as to how our predecessors managed to achieve such notable successes in the art of engineering. Their knowledge of stress analysis was rudimentary, and metallurgical science, together with heat treatment of extreme delicacy as we now know it, was practically non-existent. Yet the record of successful structures constitutes a striking testimonial to the skill of these men and their ability to reduce actual service tests to engineering design on which later construction was based.

The subjects of impact testing, temper brittleness, and aging embrittlement, have many ramifications, and a perusal of the extensive literature on these subjects discloses many inconsistencies and contradictions which are difficult to bring into agreement by any reasonable explanation, and in some cases are so opposed to each other as to arouse suspicion regarding the investigation, or question whether all the facts were taken into consideration.

To many impressed by operating conditions at 1000 degrees Fahr. (540 degrees Cent.), may we say it was not very long ago that the same condition existed in the design and construction of steam power plants for operation at temperatures between 550 and 750 degrees Fahr. (290 and 400 degrees Cent.) because carbon and chromium-nickel steels were to be used in this so-called "blue-brittle" range, and when steel is tested in this range, impact, reduction of area, and elongation drop off very sharply and fractures of steel are coarsely crystalline. In the United States alone, there are many instances of plants successfully operated within this range of temperature for more than ten years, and practically no failures have occurred.

There is no doubt that in the testing of materials, quite frequently unsupported assumptions have been liberally indulged in, and individual hypotheses advanced; but it is certain that no solution of the problem is likely to command acceptance unless backed by specific, established facts. Therefore, any theory that fits certain metallurgical problems, but is not backed by actual practice, should not be advanced.

The object of all investigation for high temperature work should be to provide a measured objective for practice and progress, in which no measurable part of the investigation should be left unmeasured, if the work is to command the confidence of those who are vitally interested in the results.

Broad conclusions must not be drawn from narrow premises, and it is therefore necessary to steer between the Scylla and Charybdis of these extremes.

The evidence substantiating the foregoing paragraphs will now be pre-

sented, particularly with reference to chromium-tungsten steel, which, on pages 932 and 938, is condemned by Mr. Wilten as temper brittle.

1. In a private communication from one of the major oil companies, we were informed that a tube of chromium-tungsten steel was brittle. In January, 1935, we received the laboratory report from this company stating that this tube was removed from the refinery after 8½ months service life at a temperature of 878 degrees Fahr. (470 degrees Cent.) and 545 pounds per square inch pressure. The tube was removed because it was crooked, but was labeled "brittle." The following is a quotation from the metallurgical report:

"Here (at their laboratory) the walls of the tube were completely flattened upon themselves under a steam hammer when the temperature of the tube material was only 60 degrees Fahr. The impact tests at room temperature also showed satisfactory ductility values."

Later, the laboratory carried out the so-called "susceptibility test" on the same tube, and when tested at 80 degrees Fahr., the quenched specimen showed 124 foot-pounds, while the furnace-cooled specimens showed 39.4, or a susceptibility ratio of 3.15. When tested at 77 degrees Fahr. the susceptibility ratio was 2.66; at 32 degrees Fahr. it was 2.46; at 0 degrees Fahr. it was 1.21; at minus 40 degrees Fahr. it was 1.08; and at 212 degrees Fahr. it was 0.94.

Therefore, the material was condemned as temper brittle, regardless of the fact that the actual tube, which had been in service for such a long period, when tested, was found to be perfectly stable. The writer's only comment at this point is that brittleness was assumed from the results of the susceptibility tests, as certainly the actual tests on the tube after removal, according to the metallurgical report, did not show it.

Again, as far as our experience and others engaged in this work is concerned, a sharp blow with a steam hammer is one of the most severe tests for brittleness in existence for reason that if brittleness does exist the metal would shatter.

2. In July, 1932, a metallurgist, whose specialty is tubes for refinery work, reported to another of the major oil companies that a state of "temper brittleness" is an inherent property of 4-6 chromium steel with tungsten, and based his conclusions on the so-called "susceptibility test," having obtained a susceptibility ratio of 1.60 by Charpy tests. The manager of construction for this company was very much disturbed over this report and dismantled a number of tubes which were sent to their metallurgical laboratory for investigation. On October 25, 1932, in a private communication, we received the following report:

"Chromium-tungsten tubes were examined at top, middle and bottom sections after service of 9252 hours, operating on Venezuelan Crude at 860 degrees Fahr. (460 degrees Cent.) and 580 pounds pressure per square inch. Impact was found to be good and rings cut from each section flattened without trouble. Metallographic examination revealed very uniform fine grain, well annealed structure entirely satisfactory. The physical properties were good, and it is apparent that 9252 hours of service at 860 degrees Fahr. (460 degrees Cent.) and 580 pounds pressure per square inch had no ill effects upon the material and it was not embrittled." He concludes as follows:

"A. That the service to which this tube was subjected had no harmful effects upon the physical properties or structure.

B. That the properties exhibited by the tube were excellent."

Little comment is necessary as regards above report.

Engineers from another large refinery reported to the writer that they were disturbed by rumors with regards to brittleness of chromium-tungsten steel, but upon investigation of chromium-tungsten tubes, which were operating at temperatures near 1000 degrees Fahr. (540 degrees Cent.) and pressures near 600 pounds per square inch for over two years, no signs of brittleness were noticeable. The test used by these people was a practical test made by striking the tube along its length with a hammer.

3. In National Petroleum News, November 16, 1932, on "Low Chromium Steels with Molybdenum or Tungsten," by W. G. Johnson, the following statement as regard to chromium-tungsten steel tubes is made:

An oil company operating on Venezuelan Crude with 1000 pounds pressure per square inch and 1050-1100 degrees Fahr. (565-595 degrees Cent.) temperature, installed a number of 4-6 chromium-tungsten tubes, and after 12,000 hours no failure occurred and no measurable corrosion could be determined. He also states that another oil company operating on Mid-Continent and Panhandle Crude with high temperature and pressure showed no loss during the time of test of over eight months on 4-6 chromium-tungsten steel tubes.

4. In a private communication we have certain figures in regard to variation of impact with temperature, which does not agree with Table VI, tube designation "E" and "F" of Mr. Wilten's paper. The figures that we quote are from a report made on tubes which had been in service as noted. Impact bars were cut from these tubes and tested with Charpy V-notch. The following are the results:

	Temperature of Test—Degrees Fahr.				
	—40	0	32	85	212
4-6 Chromium-molybdenum, Service 12 months, Pressure 525 pounds per sq. inch Temperature 880° F. Charpy Impact, ft.-lbs.	10.6	12.7	16.5	72.0	156.0
4-6 Chromium-tungsten, Service 8½ months, Pressure 545 pounds per sq. inch Temperature 878° F. Charpy Impact, ft.-lbs.	11.8	9.9	13.1	60.0	137.0

It may be well to note that this steel, when tested by the so-called "susceptibility test," showed the chromium-molybdenum to have a susceptibility ratio of 1 and the chromium-tungsten of 3.15. Yet when the material had been tested after actual service, there was practically no difference between the chromium-molybdenum and the chromium-tungsten steel in tubes.

5. We have another private communication dated July, 1933, with regards to a tube failure of chromium-tungsten steel in which it is reported that a crack was noticed after cleaning, and that part of this crack was inside the furnace and part of it outside, and that the temperature at the time of cleansing was 150 degrees Fahr. The report states that a section of a ring near the crack was cut out for a flattening test and tested at room temperature, and the slightest blow by a power hammer caused failure. Other sections of the tube

were made into rings and tested at 150 degrees Fahr., which temperature entirely removed the brittleness and the tube flattened without fracture under the steam hammer. Previous to this failure, another tube was found cracked as it was being installed and before any service operation. Of course the condition of failure of these tubes as noted in the report was blamed on temper brittleness. In the writer's opinion, it is amazing that such a report could be written and that failure concluded to be temper brittleness, when the rings showed no temper brittleness when tested at 150 degrees Fahr., yet the tube failed when cleaned at 150 degrees Fahr. The reasoning seems to be highly inconsistent.

The cause of the failure in the new tube, which was discovered on installation, was undoubtedly due to faulty heat treatment and was fortunately discovered before it had been in service, because if later discovered, would have, of course, been attributed to temper brittleness. The report further states that in annealing of the tubes, a quantity of the tubes, when piled together, might cool at a rate slow enough to induce partial brittleness. The opposite might have been the case—cooling too rapidly—as of course, this material is air-hardening.

6. The writer particularly remembers one case of tube failure that he was called upon to investigate. Someone had dropped a section of tube and it shattered. After several days of investigation as regards to physical properties of different tubes, none were found to be brittle, but upon going to the fabrication plant certain discoveries were made which would account for the brittleness that occurred. The writer watched several tubes being bent, the process being to heat the tubes to a temperature beyond the critical point, put them on a bending table and pull the ends around till the proper bend was formed, and when sufficient bending had been obtained, water from a fire hose was played on the hot tube. In other instances where localized bending was required, acetylene torches were used to heat the material beyond the critical point, bending, and then quickly quenching with a stream of water. Is it a wonder that tubes may be brittle after such drastic mistreatment?

7. In an article, "18-8 Iron, Chromium-Nickel Alloys, with Particular Reference to Its Characteristics for Cracking Coil Service," by H. D. Newell, reprint of a paper given before the American Petroleum Institute in St. Louis, April 16, 1931, p. 9, the author states:

"The impact value of low carbon 18-8 alloy prior to service is usually above 70 foot-pounds Charpy. Continued heating in cracking coil service may reduce this value to a minimum of 35 foot-pounds, which is still ample to withstand any shock likely to be met with in refinery service."

Statements by refinery metallurgists, made to the writers, have been to the effect that impact values of 20 foot-pounds on refinery tubes will never be considered as brittle.

Mr. Newell states in his paper that the usual Charpy impact on 18-8 is above 70 foot-pounds. We quite agree with him that it is above 70 foot-pounds —more likely to be above 100 foot-pounds, which, of course, dropping to 35 foot-pounds after service gives a very high susceptibility ratio, yet Mr. Newell reports in his paper that many of these 18-8 tubes have been operating 20,000 hours at temperatures of 890-930 degrees Fahr. (475-500 degrees Cent.) and

with pressures of possibly 1000 pounds per square inch. He also states that of all the tubes of this type used that probably only twenty failures have occurred, and that in twelve, which he had the opportunity to examine, failure was caused by overheating.

8. Mr. E. S. Dixon, writing in *Metal Progress,* February, 1935, page 33-36 on 5 per cent Chromium Still Tubes, heads the article, "Service Records Are Satisfactory." He states that 4-6 chromium tubes have been in service for two years and the corrosion rate was low and that they did not fail by bursting wide open without bulging. He states that type of failure experienced was similar to those of carbon still tubes. However, in Mr. Wilten's paper, on page 933, he states that carbon steel is not temper brittle and that 4-6 chromium steel is. Here is a surprising result, as it again shows that "susceptibility tests" do not check service failures, for Mr. Dixon says that tube failed similar to a carbon steel tube.

The susceptibility ratio of the 4-6 chromium steel, as given in a paper by Messrs. Wilten and Dixon, on "Aging Embrittlement of Chromium Steels," *Proceedings,* American Society for Testing Materials, Vol. 34, 1934, Part II, pages 59-78, is 4.26, while carbon steel is 0.69. The chromium-tungsten steel which Mr. Wilten reports as temper brittle in this paper was found to have a susceptibility ratio of 1.51 as reported in the previous paper of Wilten and Dixon, American Society for Testing Materials, Vol. 34, Part II.

9. In an endeavor to show that low impact values may be successfully used on material subjected to high impact and pressures, we quote an article by Langenberg and Richardson on "Significance of Impact Test," *Proceedings,* American Society for Testing Materials, Vol. 22, Part II, pages 128-136.

"It has been practice at Watertown Arsenal to take impact tests from all component parts of a gun, regardless of the ordinary tensile properties, and the acceptability of the forging as judged from this test, no piece is accepted unless results on Small Charpy impact machine show a value of at least 6 foot-pounds. In order to have a factor of safety no major forging should be accepted unless the result is at least 10 foot-pounds."

10. Wilten and Dixon, in their article on "Aging Embrittlement of Chromium Steels," American Society for Testing Materials, *Proceedings,* Vol. 34, 1934, Part II, page 59-78, Table XIII, show the following results as regards to susceptibility of several steels.

	V-Notched Specimen				
	Water Quenched		Furnace Cooled		
Type	Charpy Impact	Brinell	Charpy Impact	Brinell	Ratio
Plain Carbon	106 foot-pounds	115	155.3 foot-pounds	109	0.69
Cr_1 (4-6 Chromium)	167.3 foot-pounds	192	38.1 foot-pounds	197	4.26
$CrMo_2$ (4-6 Chromium with molybdenum)	97.5 foot-pounds	217	99.5 foot pounds	212	.98
CrW_1 (4-6 Chromium with tungsten)	178.2 foot-pounds	189	118.9 foot-pounds	195	1.51

After glancing over this report on the impact figures of the various steels as subjected to the "susceptibility test" it will be noticed that the 4-6 chromium with tungsten has the highest impact value of the chromium steels in either the water quenched or furnace cooled specimens, and while the susceptibility ratio may be somewhat higher than the chromium-molybdenum steel and carbon steel,

the impact figure of 118.9 is of the highest order, and certainly no one ever heard of a brittle steel with this impact value.

Supplementing the service information on tube material of low carbon with chromium-tungsten, we will now cite several reports in reference to casting service of similar analyses, except that carbon range is 0.20-0.30 per cent.

1. On October 7, 1932, a large power company sent us a report from which the following paragraphs are quoted:

"Recent communications from certain sources indicated that 4-6 chromium with 1 per cent tungsten steel became embrittled when subjected to high temperature for long periods of time. Because of the fact that this company had installed Chapman chromium-tungsten steel valves and fittings in connection with our high temperature units, it was thought desirable to investigate further the effects of high temperature service on such steel. A 5-inch Chapman chromium-tungsten steel valve in the outlet line of the superheater was made available for the purpose. This valve was removed after the following service:

Steam Temperature	Hours Service
900 Degrees Fahr.	504
1000 Degrees Fahr.	1,673
1100 Degrees Fahr.	10,818
Total	12,995

and delivered to the research laboratory for investigation. To assist in the interpretation of the results the tests were repeated on the same type of valve that had not been subject to service.

Conclusions

"Two statements appear to be justified as the results of the tests on the material from 5-inch chromium-tungsten steel valves:

"A. Noticeable embrittlement of the material did not occur during high temperature service.

"B. Long service at high temperature apparently resulted in an increase in toughness and ductility of the material.

"From metallographic examination of the structure, there was no definite evidence of segregation of carbides along grain boundaries in either the valve which had been in service or the one which had not been used. The distribution of carbides was more uniform in the material after service than in the unused material."

2. In another installation at a major refinery, chromium-tungsten steel valves were located on what is known as the "tube and tank cracking process" as outlet valves on soaking drums, between the drum and flash chamber at 850 degrees Fahr. (455 degrees Cent.) and 750 pounds pressure per square inch, and subjected to sulphur corrosion of West Texas Crude. In a private communication, February 2, 1934, the chief engineer of this company wrote as follows:

"Regarding the service obtained on eighteen 4-6 chromium-tungsten steel valves which you furnished in 1930 for service in the 750-pound cracking coils, would advise as follows:

"These valves were last reported on in May, 1932, and their performance has not been followed in detail since, but we are advised by the refinery that valves are still in service and have given no trouble."

We do not think it necessary to quote any further reports as to service tests, but do state that thousands of chromium-tungsten steel valves and fittings and thousands of tubes have been in service from one to five years and are functioning in a satisfactory manner without complaint as to failure from any type of embrittlement.

Before proceeding with this discussion, we believe that two statements are pertinent to this investigation, the first one taken from *Metal Progress*, Volume 22, No. 2, page 35-37, by J. M. McCloud, Ford Motor Car Company, and entitled "Laboratory Investigations are Secondary to Service Tests." Mr. McCloud states, "Service tests have sometimes demonstrated that conclusions based upon some theory evolved by laboratory work may in reality be wrong. A good example is the old Model "T" crankshaft, which for some time was made of 1 per cent chromium, 0.70 per cent manganese steel, about 300 Brinell. At times they broke by fatigue in service. On being replaced with plain carbon steel shaft of the same manganese content failures ceased. Yet the fatigue strength or endurance limit of the alloy steel at the same hardness, as used and determined in customary rotating beam machine, would be much higher than that of the simpler steel of the hardness to be found in the new shaft."

He also states, "From a metallurgical viewpoint, perhaps the main thing to be emphasized about service tests is that we must at all times realize that laboratory tests come second. They have as their function the task of measuring or appraising structures already found satisfactory in experience, so that we may therefore make others equally satisfactory."

The second statement is taken from an article by H. M. Wilten and E. S. Dixon on "American Wrought and Cast Iron in Civil War," *Metals and Alloys*, March, 1935, pages 63-66.

"From data given in Table IV a notch exerts a greater effect on wrought iron than on steel when, as a matter of fact, it is easier to break notched mild steel with a hammer than a wrought iron bar of the same size. This is another instance where laboratory tests do not corroborate the mechanical properties of wrought iron as found in actual service."

The writers could elaborate for quite some time on the service tests of material supposed to be temper brittle, but believe that sufficient evidence has been presented that the material as tested for susceptibility in the laboratory does not correspond with service tests.

In the beginning of this discussion a statement was made that a perusal of the literature showed many inconsistencies and contradictions which are difficult to bring into agreement by any reasonable explanation, and in some cases are strongly opposed to each other.

The writers will now cite some of this evidence and leave it to the members of this Society to be the final judges in this matter.

R. H. Greaves and J. A. Jones (1)*—No advantage appears to be gained by adding more than 0.5 per cent molybdenum.

Harold Tongue (2)—Careful survey of table presented by Bailey and Roberts on "Testing of Materials for Service in High Temperature Steam Plants," Proceedings of the Institute of Mechanical Engineers, Volume 122, 1932, Pages 209-284, and the report of the Chemical Industries, Ltd., Billingham, will show that molybdenum, if present in appropriate amounts, i.e., not less than 0.60, is effective in preventing temper brittleness.

*The figures in parentheses refer to the bibliography appended to this discussion.

R. H. Greaves and J. A. Jones (1)—The susceptibility of nickel and nickel chromium steels to temper brittleness is not influenced by tungsten.

E. Houdremont and H. Schrader (3)—Contrary to the results of Greaves and Jones, tungsten does tend to decrease the susceptibility of nickel-chromium steels to temper brittleness.

R. W. Bailey and A. M. Roberts (4)—Certain nickel-molybdenum steels become embrittled when subjected to stress at high temperature.

P. W. Thompson and R. M. Van Duzer, Jr. (5)—Investigation of material used in high temperature section of turbine fell definitely within range of nickel and molybdenum content, which Bailey stated was temper brittle. The results of tests at 1000 degrees Fahr. indicate that turbine material is not subject to the sort of embrittlement that Bailey encountered.

Kotaro Honda (6)—Elements chromium, silicon, nickel and phosphorus certainly promote temper brittleness, while surphur, molybdenum and tungsten do not.

J. Mussatti and A. Reggiori (7)—Research into strength as regards to static and dynamic properties, both hot and cold, caused by prolonged exposure at high temperature, a temperature of 500-900 degrees Fahr. being used. In general the best results were obtained with high nickel-chromium steel with several per cent of tungsten and 1-2 per cent silicon. Nickel-chromium, up to 35 per cent nickel and 20 per cent chromium, did not show good mechanical properties at high temperatures until the addition of tungsten was made. Replacing the tungsten with molybdenum in this type of steel did not help.

R. H. Greaves and J. A. Jones (1)—The presence of tungsten caused no appreciable change in susceptibility. Non-susceptible carbon and nickel steels remained non-susceptible. Slightly susceptible nickel-chromium steels remained susceptible to about the same degree.

J. A. Jones (8)—Impact tests made on samples of tungsten steels cooled from tempering temperature at various rates indicated that these steels (crucible melted) were not susceptible to temper brittleness. The steels tested were 0.28 per cent carbon, 1.64 per cent tungsten; 0.24 per cent carbon, 1.16 per cent tungsten; 0.30 per cent carbon, 1.72 per cent tungsten.

R. H. Greaves and J. A. Jones (1)—Chromium-nickel steel is susceptible to temper brittleness.

A. M. McKay and R. W. Arnold (9)—Embrittlement is likely to occur in steels containing 3 per cent nickel and 1 per cent chromium.

Leslie Aitchison (10)—In Table 38, Page 187, he shows a .33 carbon 3.71 nickel and .91 chromium had a susceptibility ratio of 12.5. A 0.33 per cent carbon 3.7 per cent nickel and 0.85 per cent chromium had a susceptibility ratio of 1.7; and a 0.32 per cent carbon 3.43 per cent nickel and 0.88 per cent chromium had a susceptibility ratio of 0.7. In view of the fact of the great variation in susceptibility of nickel-chromium steels, it is of course possible to obtain perfectly good toughness values for steels which have not been cooled quickly from tempering, but suggests that it is safer to assume that all nickel steels will be brittle unless cooled rapidly after tempering.

Private communication from Assistant General Manager of a large English Steel company, dated July 29, 1931.—Chromium-nickel steel is perfectly satisfactory, provided it is suitably treated, and all that one hears regarding brittleness developing in this steel is a myth.

J. H. G. Monypenny (11)—Susceptibility of steels to temper brittleness varies in different casts of nickel-chromium steel, as well as stainless. Some casts easily become brittle, while others of the same composition can be cooled at slow rates and still retain their toughness.

Private communication from the Construction Engineer of a large power plant, dated July 19, 1929.—After three years of service in ———— Station, I removed nickel-chromium steel studs which were on the steam riser just above boiler room floor at a temperature of 702 degrees Fahr. and advise that the physical tests on these studs after this long service are excellent.

A. M. McKay and R. W. Arnold (9)—Age embrittlement in steels subjected to working conditions at elevated temperature reveals itself by reduction in resistance to shock. Working stresses play no apparent part in embrittlement.

H. A. Dickie (12)—The question of stress as an accelerating factor also comes into embrittlement in practice.

A. M. McKay and R. W. Arnold (13)—Molybdenum in certain steels may retard rate of embrittlement, but molybdenum, however, will not prevent embrittlement as after a given time, its initial effect is entirely counteracted.

E. S. Dixon (14)—4-6 per cent chromium tubes do not fail by bursting wide open without bulging. Failure experienced is similar to those of carbon steel tubes.

Wilten and Dixon (15)—They report susceptibility ratio of 4-6 per cent chromium steel as 4.26, and 0.69 for carbon steel.

H. M. Wilten in present paper—Carbon steel is not temper brittle and 4-6 chromium steel is. In another private communication from a prominent manufacturing concern, it was reported that 0.35-0.45 per cent carbon steels with tungsten of from 0.66 to 2.28 per cent, and chromium from 0.57 to 1.56 per cent were tested at temperatures of 750 and 850 degrees Fahr. in their creep test machines for periods of 1145 to 2020 hours with loads varying from 12,500 pounds per square inch to 65,000 pounds per square inch. After the creep tests were completed, bars were removed from the apparatus and machined into impact bars. Impact tests were then carried out and the impact obtained after this service was checked against the original material and the susceptibility ratio was found in all cases to be less than 1. The results were obtained on not less than 15 separate tests. This same work showed a susceptibility ratio of 3.5 on a 0.40 per cent carbon with 3.5 per cent nickel, 0.65 per cent chromium steel. The date of this report was August 21, 1935.

As regards to the impact test itself, several important articles may be quoted.

J. B. Johnson (16)—The notched bar impact test for forgings has a limited application as a criterion of the quality of steel as affected by heat treatment.

J. M. Lessells (17)—With regards to impact conditions we are on insecure ground. Very little is known as to what impact values really mean. They are quite elaborate in nature and with our present knowledge can only be used as a guide of satisfactory heat treatment.

J. H. G. Monypenny (11)—Tests of ordinary carbon steels containing different amounts of carbon show that the range of "blue-brittleness" is well indicated by the notch-bar test.

H. M. Wilten in present paper, page 933—Carbon steel is not temper brittle.

F. Giolitti (18)—The results of M. Stecanelli's experiments as discussed in Metallurgia Italiana, show clearly that various technical details connected with the impact test should be submitted to extensive research before such a test can be used as an international standard.

S. L. Hoyt (19)—Notches localize the strains, and the neutral axis of a stressed bar runs close to the peak of the notch, instead of remaining in the middle section.

Rosenhain (20)—The disadvantages of using notches are—

1. Intensification of stress to the bottom of the notch.
2. They test the material only in one spot.
3. Results depend on where notch stops.

D. J. McAdams, Jr.—He recommends impact shear and gives the following reasons for so doing.

1. It applies a single kind of stress instead of a combination, as in regular impact work.
2. Un-notched specimens are used, thus removing the uncertainty of the notch.
3. One specimen can be moved along and sheared a number of times and the average results taken.

A. E. White and C. L. Clark, University of Michigan (22)—It is stated in the bibliography that the following criticisms have been made against impact testing.

1. The results of tests of two notched specimens of identical dimensions, cut from the same bar of material, might vary from each other as much as 64 per cent.
2. Results of notched bar tests are dependent upon so many factors as shape of the notch and specimens, that there is no proof results could be applied to working conditions.
3. It tests specimen only in one spot.
4. Many years use of materials of low impact value have not proved them dangerous to use in practice.

Max Moser (23)—In general, if our tests are to give reliable results the following requirements must be fulfilled:

1. The stress conditions must be similar to those which the material is required to resist in service.
2. The method of measurement must be unquestionably suitable so as to preclude introducing misleading errors.
3. The interpretation of the numerical results must be correct.

H. C. Mann (24)—The conclusions stated in a symposium on Impact Testing, held by the A.S.T.M. in 1925, may be taken to represent the present day status of the impact test (on notched bars broken transversely) from a commercial standpoint.

1. The results are not sufficiently accurate and discriminating to indicate any but rather large differences in the materials.
2. The results are in terms not applicable for use in design.
3. The results are not comparable between different types of machines.

In the present general state of knowledge, it may be well stated that very little is known as to what impact values really mean. They are undoubtedly a source of discrimination between correctly and incorrectly heat treated materials, but the results are far from acceptable as a definite measure of serviceability. In the notch bar test, the notch is used to locate the point of fracture, and the results obtained are largely dependent on the form of notch. Even when such tests are made with extreme care, duplicate tests often give widely different results, and present a serious question as to how far they should be relied upon to differentiate between physical characteristics of different materials.

F. Fettweiss (25)—Places among the disadvantages of the impact test the invalidity of the principle of geometric similarity, which may be taken to imply that conclusions as to the behavior of large sections based on results of small test pieces are inadmissible, thus rendering the test an arbitrary one, which must be carried out on a standard form of test piece.

W. George Johnson (26)—Fortunately we are not often dealing with the V-notch condition in actual refinery practice, therefore, the keyhole notch gives more reliable indication of the impact resistance of tubes.

In the paper by Mr. Wilten we find very little information as regards to the history of the material with reference to the manufacture of the steel, mechanical treatment or heat treatment. It is our belief, and concluded by others, that a very decided cause of temper brittleness or aging embrittlement may be caused by either manufacture or treatment of the steel. It seems to us that a great amount of difference in the embrittlement of steel may be caused by the method of manufacture; i.e. whether steel is made in basic or acid open-hearth or basic or acid electric furnace, for on examination of the literature, practically all investigators agree that some heats of the same analysis are susceptible to embrittlement, while others are not (refer to Leslie Aitchison (10), Monypenny (11), C. H. Herty and B. N. Daniloff (27), and W. George Johnson (26). Mr. Johnson, in particular, states that brittleness in types of steel appears to be a question of certain processes of manufacture and certain heats, rather than composition. It seems to be more liable to occur in steel made by the basic open-hearth process than the acid; and is less frequently found in steel made in the electric furnace, whereas, when melting in a crucible it is practically nonexistent). The writers have been able to check these statements in some of their recent investigations on basic and acid electric furnace steels.

Therefore, in our opinion, it is well to start at the very beginning in order to determine what may cause susceptibility. Prior heat treatment or inheritance has a very important bearing on the subject of embrittlement in alloy steels, and, in our belief, more so than any other specific cause.

Our experience has definitely shown that material apparently susceptible to temper brittleness may be rendered non-susceptible by specific heat treatment prior to the exposure for such susceptibility.

Considerable work was carried out in 1932 by Dr. Wescott and the present writers to determine the cause of brittleness in the 4-6 chromium-tungsten or chromium-molybdenum steel castings, and over 20,000 pounds of steel were made for this investigation.

In an unpublished report of this investigation, Dr. Wescott and the writers found that upon heating, there was a normal expansion of chromium-tungsten steel until a temperature of 1495 degrees Fahr. (815 degrees Cent.) was reached; at this point solution of the carbides and transformation of ferrite to austenite caused contraction in volume which persisted until the reaction was completed at 1555 degrees Fahr. (845 degrees Cent.). Normal expansion with increased temperature was then resumed. Upon cooling, the rate of contraction persisted to 1400 degrees Fahr. (760 degrees Cent.) when transformation of austenite to ferrite and precipitation of carbides was accomplished by usual volume increases until completion of the reaction at 1290 degrees Fahr. (700 degrees Cent.) when normal rate of contraction with falling temperature was resumed. The spread of 200 degrees Fahr. between the beginning of the reaction on heating and the completion of the reversed action on cooling, indicated sluggishness of the steel in response to heat treatment.

A long series of experiments was carried out to determine structural changes in the steel, which experiments provided information of the greatest value for the development of a more suitable heat treatment. Of principal interest was the data obtained in regard to the factors controlling the characteristic network formation that is nearly always present in 4-6 chromium steels, either with or without tungsten or molybdenum.

It can be definitely stated that two conditions control the structural characteristics; of these, temperature is of primary importance and time of lesser importance.

This network may be found in the ingot or casting and it is undoubtedly due to selective freezing. Subsequent cooling in the solid state and heat treatment bring about diffusion and equalization of composition in some degree, but generally not a state of complete homogeneity. With this type of steel it is therefore probable that the network consists of ferrite that is relatively rich in chromium and carbon. The chromium content of the network which may be conveniently termed chrome ferrite to agree with the nomenclature adopted for stainless steels, renders it less soluble in the etchant than the remainder of the metal and it consequently appears as a light colored constituent.

It can be stated very definitely that the network can be controlled, depending upon the heat treatment, but in reality it is merely effaced and not eradicated entirely, thereby indicating extreme sluggishness in diffusion rate in solid solution.

Where the rate of cooling is slow, the network can be shown to have a definite crystalline structure, possibly carbides much finer than in the body of the metal. With the rate of cooling slow enough to correspond to an anneal, there is a precipitation in the network of a certain constituent. Sodium picrate, used as an etching reagent, indicated a segregation of carbides in the

network of the annealed structure and a view of this dark constituent at high magnifications showed a definite crystalline structure resembling that of an eutectic. As a possible explanation of the nature of this network, it may be tentatively hazarded that it consists originally of a solid solution of segregated carbides in high chrome ferrite. Upon certain favorable conditions of cooling, the carbides are precipitated much after the manner of the insoluble phase in precipitation hardening alloys, and when steel is fully annealed they may agglomerate into larger masses which are rich enough in carbon to be stable in the sorbitic condition upon cooling.

It is possible that this agglomerated material is an eutectic between the carbides and the chrome ferrite, a supposition not incompatible with the sorbite designation.

The ideal structure in 4-6 chromium steels, with or without tungsten or

Table A
V-Notch Specimens

Type	Water Quenched (Charpy Impact)	Furnace Cooled (Charpy Impact)	Ratio
Chromium-tungsten	47.9 ft.-lbs.	34.9 ft.-lbs.	1.37
Chromium-tungsten (3% Strain)	57.0 ft.-lbs.	37.0 ft.-lbs.	1.54

Eden-Foster Specimens
(4" Drop, 5 lb. Hammer)

Type	Water Quenched	Furnace Cooled	Ratio
Chromium-tungsten	720 blows to failure	592 blows to failure	1.21

molybdenum, is clearly one of fine-grained tempered martensite or sorbite without any visible network. In order to insure the absence of the network to a harmful degree, it was evident that prolonged heating at temperature above 1600 degrees Fahr. (870 degrees Cent.) must be avoided. Because of the inherent sluggishness of the steel, it was equally evident that long soaking periods would be essential. Therefore, the most certain method of providing the necessary soaking period without promoting network formation unduly, was to carry out this portion of the treatment at a temperature slightly below the critical transformation point. In this way the steel could be brought to a uniform heat throughout and be on the verge of recrystallization without danger of network formation. This soaking period could then be followed by a normal period of heating just above the critical transformation to bring about complete recrystallization and grain refinement with minimum opportunity of segregation.

Steels which have been given this treatment and then rapidly cooled and carefully drawn back to a temperature below the critical transformation point and allowed to cool slowly to black heat have been found to possess exceptionally fine structure and physical properties, free from the erratic results obtained by usual heat treatment.

As an example of the effect of this heat treatment, the writers obtained, several months ago, sections of tube that were in the heat treated state as furnished for use in refineries. The tubing was made into Charpy V-notch impact test bars, Eden-Foster repeated impact test bars, and certain of the pieces, 15 inches long, were placed in a tensile machine and strained 3 per cent, after which they were machined into Charpy V-notch test bars. All specimens

were then heated to 960 degrees Fahr. (515 degrees Cent.) for forty hours and one set quenched in water and the other cooled slowly in furnace at the rate of 20 degrees per hour.

The results obtained are shown in Table A.

After the results shown in Table A were obtained, the tubing was re-treated in the manner as suggested in the previous paragraphs. It was then machined into Charpy V-notch impact bars, Eden-Foster repeated impact bars and strained Charpy V-notch impact bars. The material was then treated for 40 hours at 960 degrees Fahr. (515 degrees Cent.), one set quenched in water, the other set furnace cooled at the rate of 20 degrees per hour. Table B gives results of this test.

Samples of the tubing were cut into rings and treated at 960 degrees Fahr. (515 degrees Cent.) for forty hours, one set water quenched, and the other

Table B
V-Notch Specimens

Type	Water Quenched (Charpy Impact)	Furnace Cooled (Charpy Impact)	Ratio
Chromium-tungsten	85 ft.-lbs.	98 ft.-lbs.	.87
Chromium-tungsten (3% Strain)	80 ft.-lbs.	70 ft.-lbs.	1.14

Eden-Foster Specimens
(4" Drop, 5 lb. Hammer)

Type	Water Quenched	Furnace Cooled	Ratio
Chromium-tungsten	718 blows to failure	718 blows to failure	1.

furnace cooled at 20 degrees per hour, after which they were flattened under a steam hammer and in both cases the material flattened perfectly with no cracks or embrittlement. There is no doubt, therefore, in our minds, that this specified treatment has a great bearing on the so-called "susceptibility ratio."

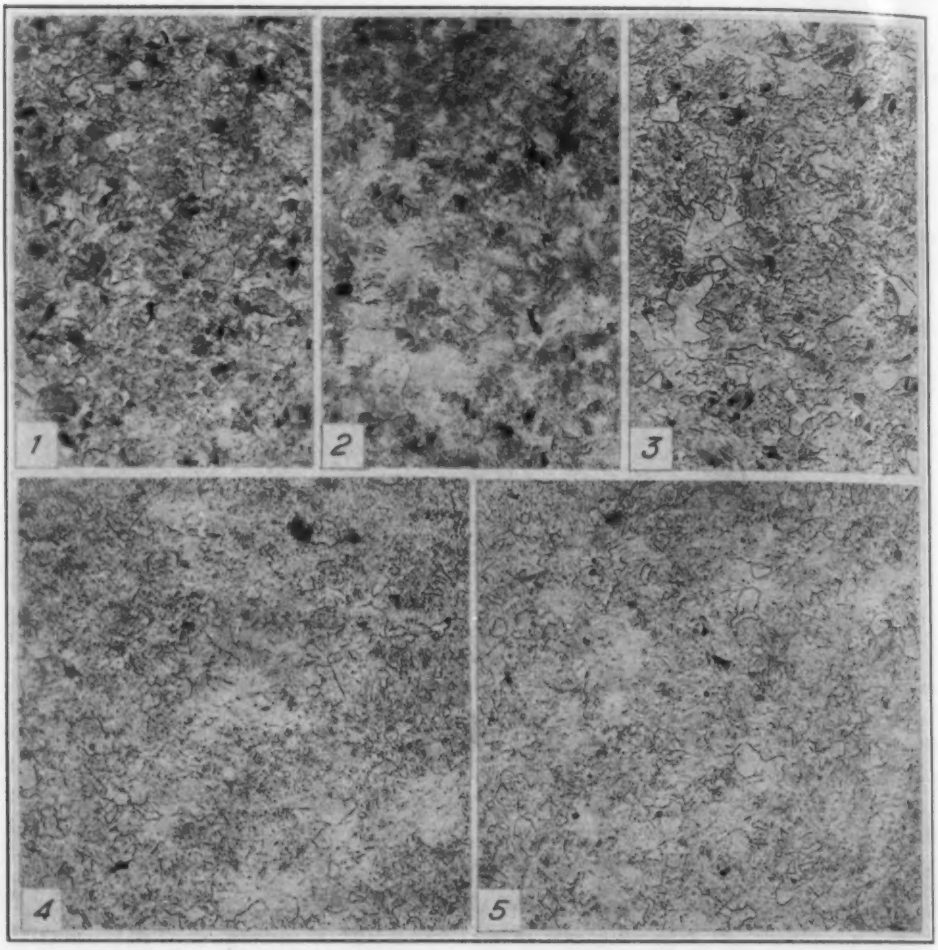
In 1932, the writers with A. B. Kinzel, chief metallurgist of the Union Carbide and Carbon Company, carried out a series of experiments on a chromium-tungsten steel tube and we were unable to find any embrittlement in this material, even though we used the susceptibility tests, the Charpy V-notch and the flattening test.

Samples of tube steel used in this investigation were made into "creep test" specimens and tested in the creep apparatus for 10,000 hours at 1000 degrees Fahr. (540 degrees Cent.) with loads varying from 4000 to 10,000 pounds per square inch. At completion of these tests, the bars were allowed to cool slowly, after which they were bent to 180 degrees without any visible signs of cracking or brittleness.

In March, 1933, we received a report from a laboratory which had made certain tests on material that had been in service and unused material. The report is as follows:

"Diffraction patterns on your samples of chromium-tungsten steel were completed and the two patterns are shown on the enclosed negatives which were obtained by surface reflection. They have been arbitrarily marked 1 and 2, as samples submitted showed no distinguishing marks.

As judged by the patterns, no difference whatever in atomic structure exists between the two specimens. They exhibit the usual alpha iron pattern with an increase in lattice parameter as compared to Armco iron, such as



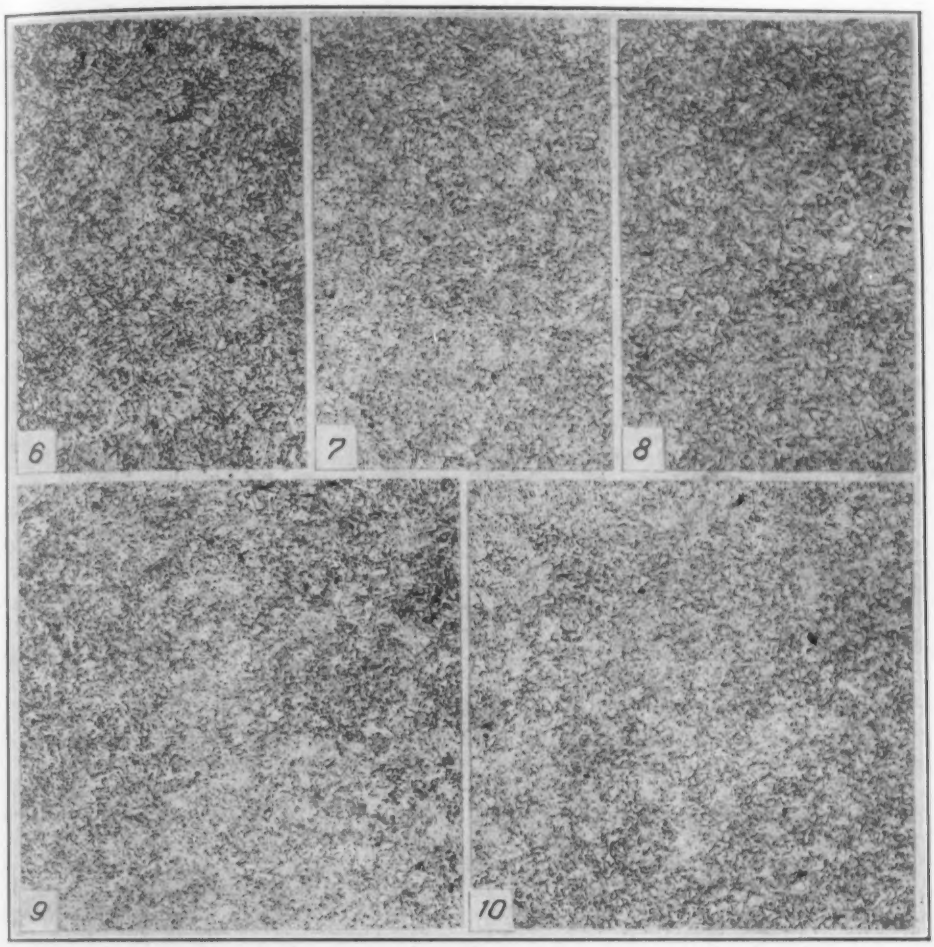
Figs. 1 to 5—Chromium-tungsten Tube Referred to in Table A. Etched with 4 per cent Nital. × 100.

Fig. 1—Material as received. Fig. 2—Tempered for 40 hours at 960 degrees Fahr.; Water-quenched. Fig. 3—Tempered for 40 hours at 960 degrees Fahr.; Furnace-cooled 20 degrees per hour. Fig. 4—3 Per Cent Strained Bar; Tempered for 40 hours at 960 degrees Fahr.; Water-quenched. Fig. 5—3 Per Cent Strained Bar; Tempered for 40 hours at 960 degrees Fahr.; Furnace-cooled 20 degrees per hour.

might be expected from presence of chromium or tungsten or the carbides of these elements."

From our studies of the heat treating of the chromium steels the mechanism of embrittlement on prolonged heating, we believe the following hypothesis to be correct, for at high temperatures there is apparently a slight solubility of the carbides in the ferrite and any treatment which will favor the production of the grain boundary network or envelopes by the expulsion of the carbides is very likely to reduce the toughness of this material when tested at room temperature.

In closing this discussion on Mr. Wilten's paper, we appreciate the very careful and painstaking work that has been done, though we believe that the



Figs. 6 to 10—Chromium-tungsten Tube Referred to in Table B. Etched with 4 Per Cent Nital. × 100.

Fig. 6—Material as retreated. Fig. 7—Tempered for 40 hours at 960 degrees Fahr.; Water-quenched. Fig. 8—Tempered for 40 hours at 960 degrees Fahr.; Furnace-cooled 20 degrees per hour. Fig. 9—3 Per Cent Strained Bar; Tempered for 40 hours at 960 degrees Fahr.; Water-quenched. Fig. 10—3 Per Cent Strained Bar; Tempered for 40 hours at 960 degrees Fahr.; Furnace-cooled 20 degrees per hour.

whole subject is controversial to a high degree, and it is true that for the present problem of design and operation, a knowledge of certain values of a given material must be determined; but are the results of these tests to limit our further advancement by placing industrial design and operation on the same basis as exacting research without definitely checking service results?

We do know that susceptibility tests are not going to be the effective solution of the problem, because we do know that hundreds of structures and many thousands of tons of steel are standing up under actual service conditions, whereas the so-called "susceptibility tests" would have immediately rejected the material.

BIBLIOGRAPHY

1. R. H. Greaves and J. A. Jones, "Temper Brittleness of Steel, Susceptibility to Temper Brittleness in Relation to Chemical Analysis," *Journal,* Iron and Steel Institute, Vol. III, p. 231-255. 1925.
2. Harold Tongue, "High Pressure Chemical Plant Design and Construction," Van Nostrand, p. 230. 1934.
3. E. Houdremont and H. Schrader, "The Question of Temper Brittleness," *Arch. f. d. Eisenhüttenwesen,* Vol. 7, p. 49-59. 1933.
4. R. W. Bailey and A. M. Roberts, "Testing of Materials for Service in High Temperature Steam Plants." *Proceedings,* Institute of Mechanical Engineers, Vol. 122, p. 209-284. 1932.
5. P. W. Thompson and R. M. Van Duzer, Jr., "High Temperature Steam Experience at Detroit," *Combustion,* November, 1933.
6. Kotaro Honda, *Metal Progress,* June, Vol. 23-6, p. 43. 1933.
7. J. Mussatti and A. Reggiori, "The Investigation of Steels Used for Valves of Explosive Motors, and Their Properties at High Temperature," *La Metallurgia Italiana,* Vol. 26, July, August, and September. 1934.
8. J. A. Jones, "Influence of Tungsten on Medium Carbon Steels Containing Nickel and Chromium," Research Dept., Woolwich Arsenal, Rep. 65. 1925.
9. A. M. McKay and R. W. Arnold, "The Effect of Time and Temperature on Embrittlement of Steels," *Iron and Coal Trades Review* (Eng.), Vol. 127, October 6, 1933, p. 517.
10. Leslie Aitchison, "Engineering Steels," Van Nostrand. 1921.
11. J. H. G. Monypenny, "Stainless Iron and Steel," John Wiley and Sons. 1926.
12. H. A. Dickie, "Embrittlement of Steel at High Temperatures," *Engineering* (London), August 4, 1933.
13. A. M. McKay and R. W. Arnold, "The Effect of Time and Temperature on Embrittlement of Steels," *Engineering* (London), Vol. 136, December 8, 1933, p. 623; and December 15, 1933, p. 647.
14. E. S. Dixon, "5 Per Cent Chromium Steel Tubes," *Metal Progress,* February, 1935, p. 33-36.
15. Wilten and Dixon, "Aging Embrittlement of Chrome Steels," *Proceedings,* American Society for Testing Materials, Vol. 34, 1934, Part II, p. 59-78.
16. J. B. Johnson, "Mechanical Testing of Aircraft Material," *Proceedings,* American Society for Testing Materials, Vol. 30, 1930, Part II, p. 119-126.
17. J. M. Lessells, Discussion of Stoughton and Harvey Paper on "Alloy Steels," *Proceedings,* American Society for Testing Materials, Vol. 30, 1930, Part II, p. 275.
18. F. Giolitti, "Shape of Impact Test Pieces," *Metal Progress,* June 1935, p. 45.
19. S. L. Hoyt, "Principles of Metallurgy," p. 223-230. 1920.
20. Rosenhain, "Introduction to Physical Metallurgy," p. 232-239.
21. D. J. McAdams, Jr., "Endurance and Impact Testing," *Proceedings,* American Society for Testing Materials, Part 16, p. 229-308. 1916.
22. A. E. White and C. L. Clark, University of Michigan, "Bibliography of Impact Testing," September 1925. Private communication.
23. Max Moser, "A New Method of Interpreting Notched-Bar Impact Results, *Transactions,* American Society for Steel Treating, Vol. 7, p. 297-320.
24. H. C. Mann, "Relation of Impact and Tensile Tests of Steel," *Metal Progress,* March 1935, p. 36-41.
25. F. Fettweiss, *Archiv für das Eisenhüttenwesen,* April 1929, p. 625.
26. W. George Johnson, "Low Chromium Steels with Molybdenum and Tungsten," *National Petroleum News,* Nov. 16, 1932.
27. C. H. Herty and B. N. Daniloff, "Cooperative Bulletin 66," Mining and Metallurgical Investigations, Carnegie Institute of Technology, Pittsburgh. 1934.

Written Discussion: By Edward R. Young, Climax Molybdenum Co.

Mr. Wilten is to be complimented on his excellent paper. It is thorough, and well summarized and it has the great merit of tying in laboratory experiment and data with actual service experience and life. Also, it seems to me

personally that his data show that, as regards the investigation of temper embrittlement, there is a great deal of merit in the well-known notched bar impact test which is often considered perhaps of questionable value.

His evidence on the value of an addition of 0.50 per cent molybdenum in improving the 4-6 per cent chromium steel as regards embrittlement is very striking and is in accord with generally accepted experience and practice. It is by far the best numerical exposition of this effect of molybdenum which has come to our attention. It is noted that the 4-6 per cent chromium-molybdenum steels which Mr. Wilten reports as still being in service have not reached the age at which he reports temper embrittlement has usually occurred in the plain 4-6 per cent chromium steel. From the evidence at hand, there is no reason to expect that the molybdenum-containing tubes, when they reach this age in service, will show any marked evidence of embrittlement, but it will be interesting to look forward to a later report on this item. The influence of molybdenum on temper brittleness has usually been stated in this rather conservative fashion: It reduces the susceptibility of steels to temper brittleness. The opinion has been expressed by some metallurgists that all steels are subject to eventual temper brittleness and that molybdenum steels apparently free from it become brittle after a long period. The length of this period has not been indicated and it is pertinent to remark here, that, even if it be true that temper brittleness eventually appears, the 4-6 per cent chromium-molybdenum steel tubes are for all practical purposes not subject to this phenomenon since the time required for its development is evidently greatly in excess of the useful life of the tube as determined by other factors, such as corrosion.

Mr. Wilten's remarks on the theory of temper brittleness and his observations on its actual apparent mechanism are very interesting and worth further study. This phenomenon has always been rather mysterious or unexplainable in any simple metallurgical fashion. We are inclined to agree with him that it has more the appearance of a peculiar condition, not yet explained, which occurs at a definite temperature rather than being caused by structural rearrangement, such as would be occasioned by carbide precipitation at the grain boundaries or age hardening dispersion effects.

The variation of impact strength with temperature and particularly low impacts in many steels at sub-zero temperature is likewise awaiting satisfactory explanation as is the fact that some alloys, such as nickel and molybdenum, improve low temperature impact values. It may well be that all these are related phenomena in that they appear to have in common the feature of being temporary values, subject to sharp fluctuations and seemingly not following as functions of any known changes in structure.

Written Discussion: By C. G. zurHorst, Gulf Research and Development Corporation.

The subject of embrittlement of 4 to 6 per cent chromium steel is one of intense interest to the producers of tubes for refinery service and to those connected with refinery operations, since such failures, if not discovered on cold oil or steam tests, might result in losses amounting to thousands of dollars in addition to endangering the lives of the workmen.

Examinations of new tubes, tubes after thousands of hours of service and tubes which have failed in service, did not reveal any great differences in metal-

lographic structure, tensile strength or ductility. The only property which was found to differ greatly was the Charpy impact value.

In investigations of embrittlement failures of straight 4 to 6 per cent chromium tubes, the only material in which failures were obtainable, and of new and used tubes containing both molybdenum and tungsten as additional alloys, both methods mentioned by Mr. Wilten to determine the degree of embrittlement and the susceptibility of the material to embrittlement were employed. To determine the degree of embrittlement, impact tests were made at room temperature and also at 200 degrees Fahr. The ratio between these values was taken as the degree of embrittlement. The susceptibility of the material to embrittlement was found by determining the ratio between the impact value of the material after slow cooling (20 to 35 degrees Fahr. per hour until 700 degrees Fahr. is reached) from 1175 degrees Fahr. (635 degrees Cent.) and the impact value of the material when water quenched from this same temperature. Unfortunately all of the values upon which ratios herein mentioned were obtained, were secured on specimens of the usual key hole type and are not comparable to those given by Mr. Wilten.

Susceptibility ratios determined on sections of new tubes were found to be as follows: Chromium-molybdenum, 1.00; Chromium (Straight), 1.12; Chromium-tungsten, 1.44. This would indicate that failures of chromium-tungsten tubes should out number those of the straight chromium materials which is decidedly incompatible with experience.

Examinations of tubes which had been in service from 9000 to 15,000 hours without failure, showed embrittlement ratios of from 1.05 to 1.35. These were of the straight chromium and chromium-tungsten types. Though they exhibited some increase in impact value, when tested at 200 degrees Fahr., they could not be classed as brittle when tested at room temperature. The minimum value found at room temperature was 38.6 foot-pounds which certainly would prohibit them from being considered brittle. The highest value found in these tests was 62.4 foot-pounds. Attempts to appreciably embrittle them by slow cooling from 1175 degrees Fahr. (635 degrees Cent.) were unsuccessful.

Examinations of tubes which failed after various periods of operation resulted in embrittlement ratios of from 1.56 to 7.1. These tubes were all of the straight 4 to 6 per cent chromium material and could truly be considered embrittled when tested at room temperature, since the values found were as low as 3 foot-pounds. In all instances, failure was discovered upon cold oil testing before returning the unit to operation, and unquestionably resulted from the battering received during the cleaning operations.

From Mr. Wilten's paper and from other investigations it appears that only some of the tubes are capable of being rendered brittle at room temperature. This prompts the thought that susceptibility to embrittlement, whatever its cause, may be an inherent property of certain tubes or heats of steel. It has been possible, by proper heat treatment, to impart a good impact value to a tube which had failed from embrittlement, and it has also been possible, by slow cooling from 1175 degrees Fahr. (635 degrees Cent.) to re-embrittle this same material. However, attempts were unsuccessful to embrittle appreciably cer-

tain other new tubes or tubes which had been removed from a unit without failure after thousands of hours of service.

Supporting evidence that susceptibility to embrittlement is a property of the individual tube or heat and not of the material as a class, has been encountered. One straight chromium tube which had been in service for 11,000 hours and was removed without failure, possessed an impact value of 62.4 foot-pounds at room temperature. The impact values after slow cooling and quenching from 1175 degrees Fahr. (635 degrees Cent.) were 54.5 and 62.0 foot-pounds respectively, giving a susceptibility ratio of 1.14. This tube was apparently not capable of appreciable embrittlement. Another tube of this same material showed an embrittlement ratio of 1.05 after 15,855 hours' service. This tube was also removed without failure for examination.

Two chromium-tungsten tubes were removed for examination after 14,167 hours and 9252 hours' service respectively. The first of these had an embrittlement ratio of 1.19 and the second had impact values above 40 foot-pounds at room temperature. No ratios were determined on this latter tube, but it certainly could not be considered brittle.

A straight chromium tube which failed after 7779 hours had an impact value of 7.5 foot-pounds at room temperature. Tests on this material revealed an embrittlement ratio of 3.51. Pieces of this tube were then annealed at 1750 degrees Fahr. (955 degrees Cent.), after which the impact value at room temperature was found to be 30.1 foot-pounds. Quenched and slow cooled specimens of this annealed material gave 11.6 and 31.8 foot-pounds respectively for a susceptibility ratio of 2.74.

Thoughts of an investigation to definitely determine whether susceptibility to embrittlement is a property of a material as a class or of the individual tube or heat have been entertained for some time, but the work has never been started. If it were definitely proven to be a property of the individual tube or heat susceptibility tests could then be made on each tube prior to acceptance at the manufacturer's plant, and thus eliminate receipt of tubes subject to embrittlement. If on the other hand, it is found to be a property of the material as a class, which appears to be accepted without absolute proof, then the use of that material should be avoided for refinery tube service.

All of the failures from embrittlement thus far reported have been encountered at atmospheric temperatures, and have resulted from the severe battering necessary to remove the hard coke deposits on the inside of the tube. Since the embrittlement is relieved at a slightly elevated temperature (only 200 degrees Fahr.) the chances of failure at operating temperatures of tubes, susceptible to embrittlement, are extremely slight, and it appears that, for the present at least, or until such time as the cause of this embrittlement can be definitely determined and guarded against, cleaning of still tubes should be done at temperatures in the region of 200 degrees Fahr.

I am certain that it will be generally agreed that this paper presented by Mr. Wilten is a valuable contribution to the present rather meager supply of information available on these particular steels and it is hoped that it will stimulate further investigation of the phenomenon of high temperature embrittlement. Mr. Wilten is to be congratulated on the thoroughness and extent of the investigational work leading to the results reported in his paper. These

results furnished decidedly interesting and valuable information for study, and, while all of the conclusions given may not be accepted without some reservations on the basis of information now available, it is certain that they provide a means for the selection of medium alloy steel for high temperature service with assurance that failures from embrittlement will be restricted to a minimum.

Oral Discussion

P. PAYSON:[1] Since we sell both the chromium-molybdenum and chromium-tungsten steel, I would not want to say one is better than the other. We have had experiences where both have been giving excellent service. I know of one case where the tungsten steel has been in service as a stud in a power plant operating at 850 degrees Fahr. (455 degrees Cent.) for two and one-half years, and the studs are still giving quite satisfactory service. About two years ago there was a suspicion that they might fail, so some studs were taken out and tested, and since then we have tested them at intervals of about a year. Although the notch impact is quite low the toughness value has not gone down in the last two years.

We know that the molybdenum addition decreases susceptibility to temper brittleness. Houdremont and his associates in Germany showed about three years ago that although they could not arrive at a satisfactory explanation, they did find that it is a fact that a molybdenum addition does decrease the tendency to temper brittleness.

One point I think might have been overlooked by tube mannfacturers, and that is the effect of initial condition of the material on its subsequent behavior in service. In a series of laboratory tests with both the molybdenum and tungsten steels, we found that if the material was in a lamellar pearlite condition before it was subjected to long time heating at about 800 to 1000 degrees Fahr. (425 to 540 degrees Cent.) and then subjected to tests at sub room temperatures, the material had a lower impact value than if it had been annealed to a spheroidized condition before it was subjected to the long time heating. I think the tube manufacturers should bear that in mind. I think also that if they check our tests, they will find it of value to specify that tubes should be annealed to a spheroidized condition, rather than a lamellar condition, before being put in service.

R. L. WILSON:[2] In reviewing the extensive work covered by this most interesting paper, I was particularly impressed with the fact that 4 to 6 per cent chromium steel in the brittle condition should show such a rapid rise in impact strength on being heated from room temperature to 212 degrees Fahr. There is associated with this change the idea that the impact resistance of the steel increases with temperature, and also that the susceptibility ratio for temper brittleness changes with temperature. From Tables V and XVI there is at least the implication that this behavior of the 4 to 6 per cent chromium steel in the brittle condition is a manifestation of temper brittleness. I believe it is commonly accepted that temper brittleness is ascribed to the solubility of carbide in alpha iron, the later precipitation of carbide on heating, the globularization of the carbide particles so formed, and perhaps the expulsion of the car-

[1]Crucible Steel Company of America, New York City.
[2]Timken Steel and Tube Company, Canton, Ohio.

bide to the grain boundaries in the structure. As far as I am aware, nobody has been able to trace any effects of carbide precipitation on temper brittleness under a temperature of about 450 degrees Fahr. (230 degrees Cent.). I therefore wonder whether this behavior of the 4 to 6 per cent chromium steel in the brittle condition might not simply be the result of change in impact value with temperature, rather than having any direct connection with temper brittleness.

Author's Closure

The author is gratified at the interest shown in his paper.

With reference to discussion by Messrs. Malcolm and Jones, the author wishes to state that he did not intend to condemn chromium-tungsten steel. The company with which the author is associated has many valves of chromium-tungsten steel in service with thus far excellent service records. He showed, however, that in line with some plain 4 to 6 per cent chromium steels, chromium-tungsten failures due to embrittlement correlated with the temper brittleness test. Personally, the author votes for chromium-molybdenum analysis, basing his opinion on lack of failures due to the embrittlement in practice as well as on the laboratory tests presented.

The writer purposely used a term of embrittlement to designate these particular failures as those which "differ radically from other types of failures under combined stress and temper." That was also his reason for calling these "abnormal, brittle failures." The author wishes to assure Messrs. Malcolm and Jones that in these failures true shattering has occurred. To illustrate further the difference in the condition of metal the following experiment is cited. If a portion of a tube which failed due to embrittlement and which does not contain any cracks (shown by etching in acid) be subjected to knocking action of a cleaning apparatus the tube metal can be split in the manner shown in Fig. A of this closure. If a portion of a tube which failed at high temperature be subjected to the same test, no such splitting is likely to be produced. In fact the metal is actually bulged as shown in Fig. B. In this case the metal is in a ductile condition, while in the former case it is in an embrittled condition.

Item 5 of their discussion states, however, that the chromium-tungsten tube was found cracked after cleaning. This is what the refinery operator does not want to occur. It does not make any difference to him whether chromium-tungsten steel is temper brittle or not. He wants a tube metal that will not be subject to such failures, and he finds it in chromium-molybdenum analysis. It happens that the author finds correlation between such failures and the temper brittleness test and so far the service facts substantiate this correlation.

In Item 8 they refer to Mr. E. S. Dixon's statement that type of failures of 4-6 per cent chromium steel tubes is similar to those of the carbon steel tubes. Mr. Dixon referred to similarity of failures at high temperatures. We never found carbon steel tube metal temper brittle and we never had a failure such as shown in Fig. 2 in the manuscript. Mr. Dixon agrees with the author on the mode of failures of the carbon and chromium tubes at high and low temperatures.

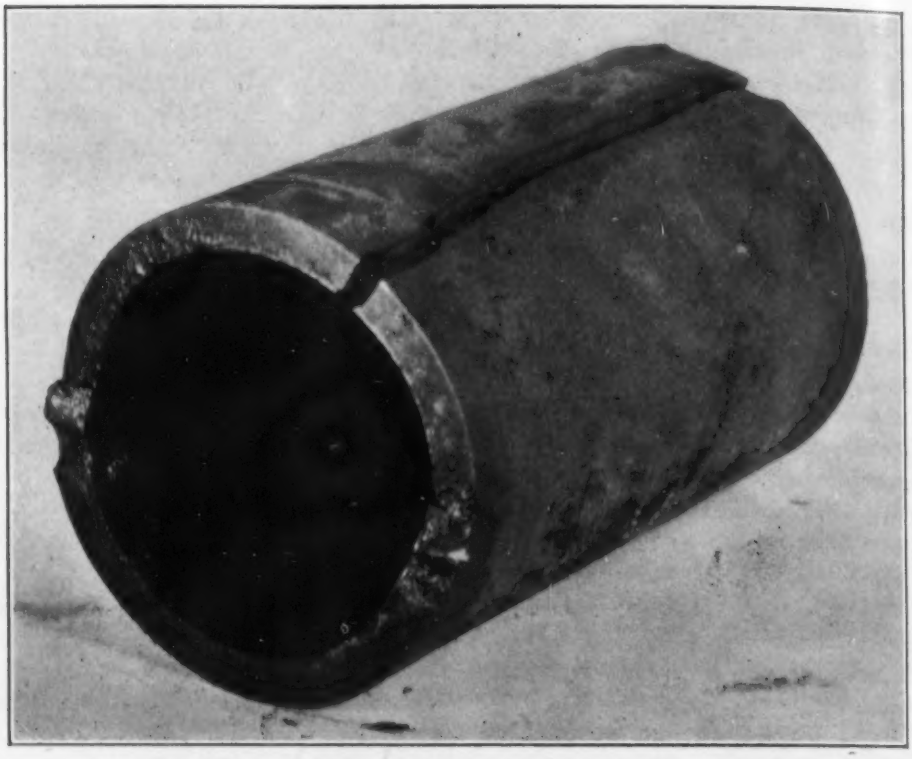


Fig. A—Split Produced Experimentally with a Tube Cleaning Device.

The author is well aware of the limitation and the controversy regarding the use of the notched bar impact test. He realizes that the results of impact tests are profoundly influenced by the change in size of specimens; by the change in depth of notches and their shape. The test, however, must be useful otherwise it would not have been so widely adopted. Furthermore, if the metallurgist is guided by the trend of the impact values and checks the test data with the facts obtained in service he can derive very useful information. The author believes that in the particular use of 4 to 6 per cent chromium type steels in the oil refinery, the notched bar test, and, particularly the purely laboratory temper brittleness test, he can evaluate the comparative quality of these steels for this service in a practical manner. The author wishes to thank Messrs. Malcolm and Jones for including a complete bibliography on this subject and he finds their discussion of the effect of manufacture and heat treatment on the properties of steel very enlightening.

Regarding Mr. Newell's recommendation to use a ring test, the author had used the same test in the past, but discarded it due to the fact that the embrittled tubing usually had residual internal stress which complicated the test to such an extent that the true brittleness could not be determined. While it is true that by simple laboratory experimental heat treatment one can lower the impact value of these steels very considerably, actually, in service, time factor appears to be of considerable importance. Table VI in the test shows the change in properties in chromium-molybdenum tubes which were in service 4½ months. The data are now available on the change in properties of tubes

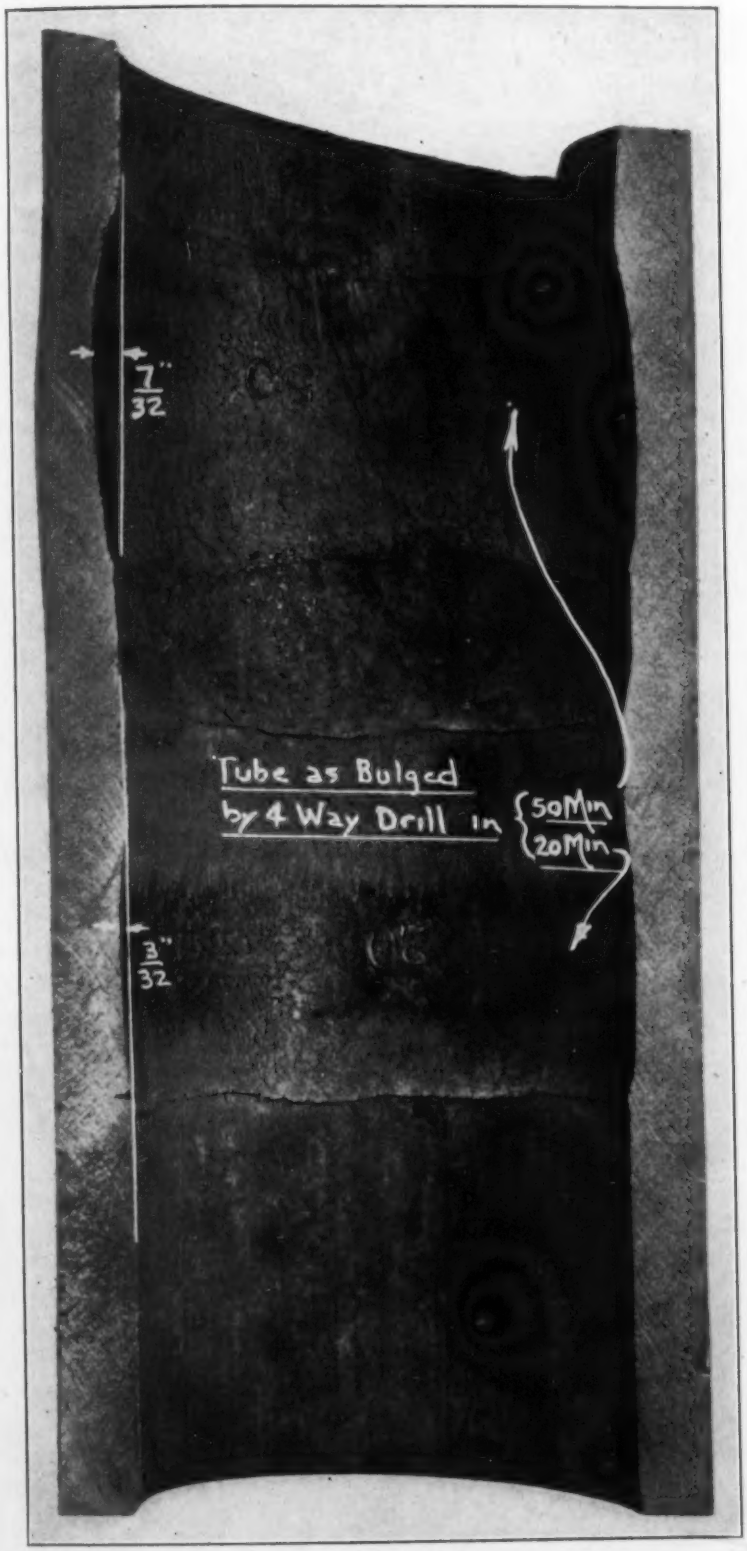


Fig. B—Tube Bulged Experimentally with a Tube Cleaning Device.

from the same heat which were in service a year and four months. These are shown in supplementary Tables VI-A and VII-A and these figures should be compared with the original Tables VI and VII in the text.

Table VI—A Supplementary
Effect of Service on Tensile Properties of Tube Metal of 4 to 6 Per Cent Chromium Steel Plus Molybdenum

Tube Designation	Section	Tensile Strength Lbs./Sq. In. Original	Tensile Strength Lbs./Sq. In. After Service	Elongation in 2" Per Cent Original	Elongation in 2" Per Cent After Service	Reduction of Area Per Cent Original	Reduction of Area Per Cent After Service	Brinell Original	Brinell After Service
H	Front	72600	73000	33	32.5	60.8	70.8	...	...
H	Back	73700	71400	30	32.5	68.6	70.6	...	...
J	Front	76800	71600	33	31.5	70.2	70.3	143	128
J	Back	73900	65800	32.5	33.0	70.0	71.0	143	128

Effect of Service on Impact Properties of 4 to 6 Per Cent Chromium Steel plus Molybdenum.

Tube Designation	Section	Charpy Ft-Lbs. Izod Notch Original	Charpy Ft-Lbs. Izod Notch After Service	Brinell Hardness Original	Brinell Hardness After Service
H	Front	130.9	58.4	134	114
H	Back	107.8	34.3	134	114
J	Front	120.6	36.6	129	117
J	Back	106.5	52.0	138	121

Variation of Impact Property with Temperature.

Tube Designation	Charpy Ft.-Lbs. Izod Notch −40° F. (−40° C.)	0° F. (−18° C.)	32° F. (0° C.)	85° F. (30° C.)	212° F. (100° C.)
H	.....	....	34.6	58.4	....
J	21.7*	41.2	85.4	120.6	....

*Very erratic. Values were 40.8, 32.9, 8.5, 4.7.

Table VII—A Supplementary
Temper Brittleness Susceptibility

Tube Designation	Temperature	Quenched Specimens Charpy Ft-Lbs. Izod Notch	Quenched Specimens Brinell	Furnace Cooled Specimens Charpy Ft.-Lbs. Izod Notch	Furnace Cooled Specimens Brinell	Ratio
H	0° F.—(−18° C.)	156.8	...	160.9	...	.97
H	32° F.—(0° C.)	151.4	...	175.0	...	.865
H	88° F.—(31° C.)	147.4	201	166.0	192	.89

We have no theory available at this time to explain why the impact properties of the steel from the same heat improved after 4½ months service and again were found deteriorated after a year and four months service. It has been already stated in the text that the laboratory stability test did not show any difference in behavior of chromium steels and those alloyed with molybdenum. Both types of steel lost their impact resistance. Bailey and Roberts (5) have also found that it is necessary to have at least 0.7 per cent molybdenum to prevent embrittlement under their experimental procedure. It has occurred to the author for some time that the present arbitrary limit of 0.40 to 0.60 per cent molybdenum in chromium steel should be revised upwards to further retard any chance of embrittlement of these steels in service. The author agrees with Mr. Newell's observation on the importance of the grain-size on the notch impact value of these steels. He questions, however, the statement that the suppression of brittleness is due to the refining action of molybdenum on the grain-size, in view of the fact that both tungsten and vanadium have a

greater refined action on the grain-size and neither has the retarding influence on temper brittleness that the molybdenum has.

Mr. Payson's suggestion regarding the specification that tubes should be annealed to a spheroidized condition is worth considering. At any rate the steel of this analysis tends to spheroidize on annealing. In fact very little difference is usually found in the structure of new tubes and tubes used in service for several thousand hours. This is confirmed by Mr. C. G. zurHorst.

Mr. Young's conservative statement on the effect of molybdenum addition to the chromium steels is fully endorsed by the author. The fact that chromium steels alloyed with molybdenum show some decrease in impact value with service, may not be of great practical importance. Considerable loss of impact resistance has also been encountered in plain carbon tubes. This test is plainly more searching and sensitive than the laboratory temper brittleness test. This fact is also confirmed by the researches of E. Houdremont and H. Schrader (14) page 54, who state that tempering at 500 degrees Cent. (930 degrees Fahr.) can develop temper brittleness in many steels, which would be considered immune against this disadvantage by the method of evaluating the ratio of impact resistance after tempering of oil quenched and furnace cooled steels.

Replying to Mr. R. L. Wilson the author wishes to point out that the change in plasticity of ordinary low carbon steel is abrupt, both for the impact and the tensile tests, (11) so that there is nothing singular about this steel to rise rapidly in the impact test from room temperature to 212 degrees Fahr. The rapid rise in impact at this comparatively low temperature is what makes the author doubt the precipitation theory for temper brittleness as applying to these steels. If the definition of temper brittleness be applied to the phenomenon of change of impact value with tempering, say at 500 degrees Cent. (930 degrees Fahr.) (for a long interval of time) then we must assume that temper brittleness results in some atomic or molecular change in the steel itself, since there is no change of temperature involved.

Responding to Mr. C. G. zurHorst the author believes that temper brittleness is an inherent property of certain heats of steel. This is not only true of the temper brittleness property, for other properties vary from heat to heat, for example cold shearing properties of steel of practically the same analysis may show enough variation as to cause inconvenience and necessitate different set up of shears. As a class, for example, certain analyses may show susceptibility to temper brittleness—more so than other steels, Table XVI of this paper shows one heat, (1), of 4-6 per cent chromium steel that shows no embrittlement susceptibility. This, moreover, is not an isolated occurrence. The author does not believe that susceptibility to embrittlement is a property of the individual tube. There is a preponderance of metallurgical data supporting the theory that the properties of steel of individual heats are characteristic throughout the heat. For example, H. W. McQuaid (15) reports that addition of very small percentage of aluminum to a large heat of steel results in uniformity of grain-size control throughout the heat. The author hopes as a result of his studies of correlation of the embrittlement test with the service failures that this test will prove to be of value in predicting the service properties of steel in the oil refinery service just as McQuaid-Ehn test is widely used today in automobile engineering to determine the response of the steel to processing.

CHROMIUM STEELS OF HIGH NITROGEN CONTENT

By Russell Franks

Abstract

This paper discusses the influence of nitrogen in steels of high chromium content. The observations strongly indicate that the marked refinement of grain imparted to the high chromium steels is brought about by nitrogen that is believed to be in combination with chromium as a nitride. Chromium nitride representing only a few hundredths of a per cent greatly increases the hardening capacity of low carbon 12 to 14 per cent chromium steels, a good indication that this nitride promotes austenite formation. The effect of this high solubility of the chromium nitride in low carbon iron of greater chromium content is far more pronounced, and in this respect the chromium nitrides seem to function in a manner similar to that of the carbides in ordinary steel. The addition of nitrogen to these low carbon-high chromium irons represents therefore a practical metallurgical procedure designed to limit grain-size and to improve strength and toughness without unduly increasing hardness associated with brittleness, a result invariably obtained when carbon is employed for a similar purpose.

SINCE the publication[1] of data pertaining to the effects of nitrogen in high chromium steels, references have been made to the peculiar phenomenon involving the use of an element normally gaseous to refine the grain structure of metals. It is pertinent to state in beginning the present discussion that the function of nitrogen is undoubtedly of a different nature, and a few explanatory remarks seem worth while.

The observations strongly indicate that the beneficial effects are brought about by nitrogen[2] that is believed to be in combination with chromium as a nitride, which behaves in many respects similar to a

[1] "Chromium Steels Improved by Nitrogen," by Russell Franks, *Iron Age*, Sept. 7, 1933.

[2] "The Effect of Nitrogen on Chromium and Some Chromium Iron Alloys," by Frank Adcock, *Journal*, Iron and Steel Institute, No. 2, 1926.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The author, Russell Franks, is research metallurgist, Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, N. Y. Manuscript received June 1, 1935.

carbide. A fact well-known is that when carbon is introduced into ferritic iron increased strength, ductility, and toughness resulting from control of grain-size may be imparted to the metal by proper thermal treatment, or depending upon carbon content the product may be rendered quite brittle. That the properties of these carbon steels can be so greatly changed by thermal treatment is believed to be due to the ability of the carbides formed to develop austenite on heating within certain known temperature ranges, thereby influencing grain-size.

When about 12 per cent chromium is incorporated in these steels the hardening ability of a given percentage of carbon is markedly enhanced even though the percentage of carbon in the steel is relatively low (0.10 per cent or lower). Low carbon steels containing these percentages of chromium have excellent ductility and toughness associated with relatively fine grains, if annealed under the proper conditions. A gradual increase of chromium content beyond 12 per cent produces decidedly different results in these low carbon steels. The carbides formed in the higher chromium ferrite do not readily develop an austenitic constituent which decomposes under the influence of temperature changes permitting at the same time a control of grain-size. It must not be construed from these statements that it is impossible to develop the austenitic constituent in a plain 18 per cent chromium steel by an increase of carbon content. It is appreciated that this can be done but a decrease in corrosion resistance takes place and the steel is not especially ductile or tough, and it is too hard and brittle for many purposes. The presence of 20 per cent or more chromium further decreases the tendency to form austenite, and from a practical standpoint the low carbon steels of this class may be considered to be truly ferritic, possessing therefore relatively large grains that are susceptible to growth on exposure to high temperatures, and a reduction in grain-size can be obtained only by mechanical working.

The marked effects of nitrogen in the form of chromium nitride on the low carbon-high chromium ferrites may now be considered in view of the previous statements referring to the action of carbon in combination as carbide. Chromium nitride representing only a few hundredths of a per cent of nitrogen greatly increases the hardening capacity of a 12 per cent chromium steel of given carbon content, a good indication that this nitride promotes austenite formation. The effect of this high solubility of the chromium nitride in

low carbon iron of greater chromium content is far more pronounced, and in this respect the chromium nitrides seem to function in a manner similar to that of the carbides in ordinary steel. The addition of nitrogen to these low carbon-high chromium irons represents therefore a practical metallurgical procedure designed to limit grain-size

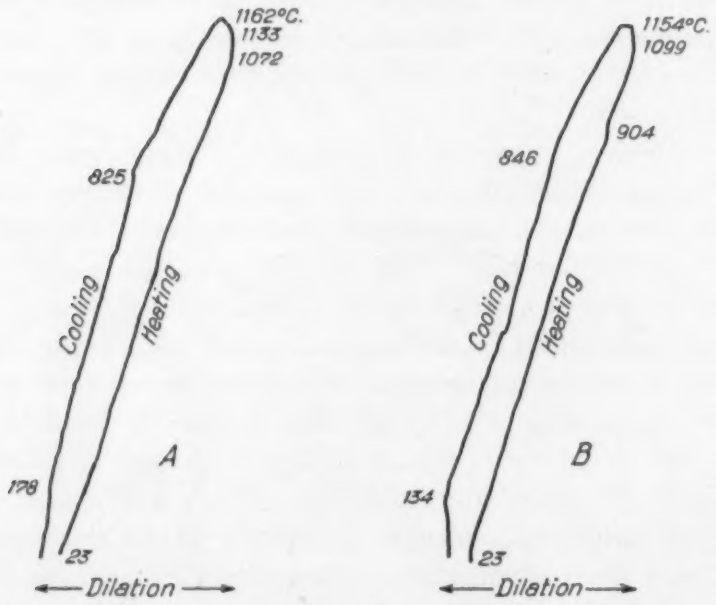


Fig. 1—Critical Point Determinations Revealing the Influence of Nitrogen on the 18 Per Cent Chromium Steels. A—This Steel Contains 18.77 Per Cent Chromium and 0.10 Per Cent Carbon. The Changes That Occur on Heating and Cooling This Steel from 1162 Degrees Cent. (2120 Degrees Fahr.) Are Not Well Marked. B—There Are Rather Definite Change Points in This Steel Which Contains 18.45 Per Cent Chromium, 0.08 Per Cent Carbon, and 0.17 Per Cent Nitrogen.

and to improve strength and toughness without unduly increasing hardness associated with brittleness, a result invariably obtained when carbon is employed for a similar purpose.

The striking influence of nitrogen on the thermal characteristics of the high chromium steels is illustrated in Fig. 1. Curve A reveals that a normally low nitrogen, low carbon 18 per cent chromium steel expands and contracts on heating and cooling with only slight indication that a critical change takes place on cooling, while Curve B shows definitely that changes occur in a high nitrogen steel of similar chromium and carbon contents. The change to be noted in Curve A is undoubtedly due to the fact that the steel was heated to 1162 degrees Cent. (2125 degrees Fahr.), at which temperature a small amount of carbide goes into solution and begins to precipitate

on cooling when a temperature of 825 degrees Cent. (1515 degrees Fahr.) is reached. In the instance of Curve B a solution of nitride or both nitride and carbide takes place on heating at 904 degrees Cent. (1660 degrees Fahr.), and on cooling precipitation starts at 846 degrees Cent. (1555 degrees Fahr.), revealing that critical changes do occur.

Nitrogen has been employed commercially in cast steels containing more than 20 per cent chromium to secure decreased grain-size,[3] and invariably an improvement in strength and toughness has been obtained. The nitrogen in combination as a nitride is added as a ferrochromium alloy containing approximately one part of nitrogen to one hundred parts of chromium, and the high nitrogen steels can be made without difficulty provided the proper precautions are taken. The beneficial effects of nitrogen are obtained in the steels containing in excess of 20 per cent chromium if the nitrogen is present to the extent of 1 part to 100-180 parts of chromium. In steels of the 12 and 18 per cent chromium variety the nitrogen should be in the ratio of 120-200 parts of chromium to 1 part of nitrogen, the smaller percentages of nitrogen being most effective in the lower chromium wrought steels. The question may be asked as to why larger ratios of chromium to nitrogen are suggested for the lower chromium steels. This may be answered by the statement that the chromium nitrides are less soluble in the lower chromium steels.

Only a few comments will be made in regard to the effects of nitrogen on the properties of cast chromium steels. Data based on commercial work show that the strength and toughness of these steels are greatly improved by the presence of the proper percentages of nitrogen. The important effect of nitrogen on the grain-size of the cast 25 per cent chromium steel is illustrated in Fig. 2. These castings were made under commercial conditions using dry sand molds, and the figures are of natural size. It is shown that even the two- and three-inch round bars of the high nitrogen 25 per cent chromium steel are composed of much smaller grains than the one-inch bar of low nitrogen steel of similar chromium content, and as a result of this improvement in grain structure the strength of the steel in both the transverse and longitudinal directions is increased appreciably. These improvements are attained without detrimentally affecting resistance to oxidation at elevated temperatures or decreasing corro-

[3] "Effect of Nitrogen Content on High Chromium Steels," by S. M. Norwood, *Canadian Chemistry and Metallurgy*, Vol. XVIII, No. 2, 1934.

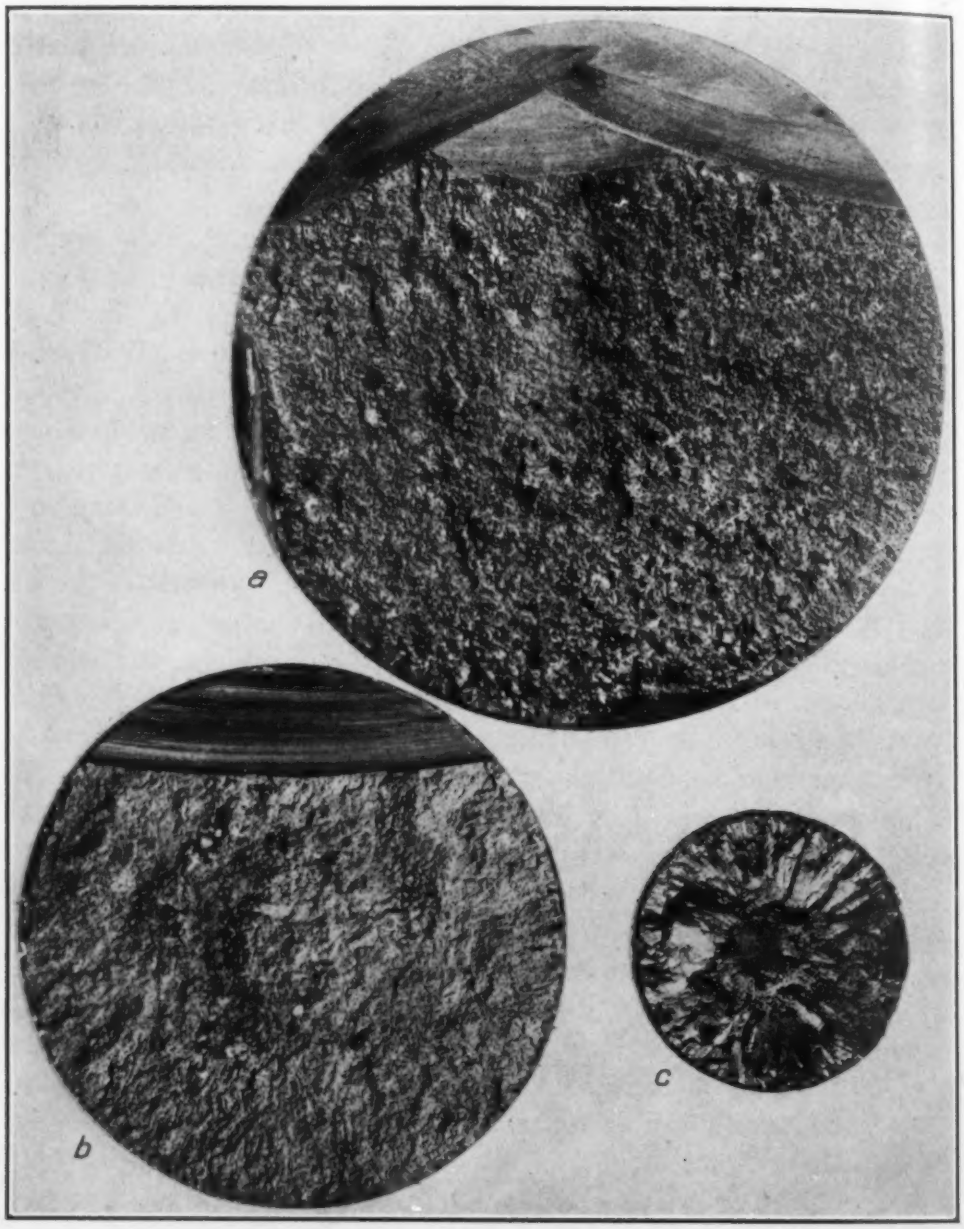


Fig. 2—Fracture of Cast High and Low Nitrogen 25 Per Cent Chromium Steels. a—Fracture of Cast Three-Inch Bar of a Steel Containing 24.73 Per Cent Chromium, 0.35 Per Cent Carbon, 1.25 Per Cent Nickel and 0.25 Per Cent Nitrogen. Actual Size. b—Fracture of Cast Two-Inch Bar of Same Steel. Actual Size. c—Fracture of Cast One-Inch Bar of a Steel Containing 25.08 Per Cent Chromium, 0.35 Per Cent Carbon, 1.18 Per Cent Nickel and 0.04 Per Cent Nitrogen. The Grains of This Steel Even in a Smaller Section Are Considerably Larger Than Those of the High Nitrogen Steels. Actual Size.

sion resistance as measured by nitric acid or weak solutions containing a mixture of nitric and sulphuric acids. The addition of ap-

Table I

Physical Tests on Wrought High and Low Nitrogen 13 Per Cent Chromium Steels

Standard Samples Taken from 1 Inch Round Bars

Per Cent Cr	Per Cent C	Per Cent N	Condition of Metal**	Yield Point Lbs. Per	Max. Stress Sq. Inch 2	Per Cent Elongation in Inches	Per Cent Reduction of Area	Izod Impact Ft.-Lb.	Brinell Hardness
*13.44	0.07	0.025	Oil-quenched from 950 degrees Cent. (1740 degrees Fahr.)	139,000	151,000	10	15	5	293
*13.44	0.07	0.025	Oil-quenched from 950 degrees Cent. (1740 degrees Fahr.). Held 2 hours at 600 degrees Cent. (1110 degrees Fahr.) and air-cooled.	66,000	95,500	23	60	58	187
*13.44	0.07	0.025	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	44,000	78,500	30	71	101	137
*13.19	0.07	0.08	Oil-quenched from 950 degrees Cent. (1740 degrees Fahr.)	178,000	194,000	5	11	4	402
*13.19	0.07	0.08	Oil-quenched from 950 degrees Cent. (1740 degrees Fahr.). Held 2 Hours at 500 degrees Cent. (930 degrees Fahr.) and air-cooled.	.....	.....	..	..	..	387
*13.19	0.07	0.08	Oil-quenched from 950 degrees Cent. (1740 degrees Fahr.). Held 2 hours at 550 degrees Cent. (1020 degrees Fahr.) and air-cooled.	.....	.....	..	..	..	311
*13.19	0.07	0.08	Oil-quenched from 950 degrees Cent. (1740 degrees Fahr.). Held 2 hours at 600 degrees Cent. (1110 degrees Fahr.) and air-cooled.	106,500	123,500	21	65	60	228
*13.19	0.07	0.08	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	66,500	90,500	26	66	100	179

*The steel also contains normal percentages of silicon and manganese.

**Samples fully softened before hardening and tempering.

proximately 1 per cent nickel has been made to castings of these high nitrogen 25 per cent chromium steels, and while this element is not entirely essential some additional improvement is obtained.

The effects of nitrogen in the low carbon wrought chromium steels are interesting from many viewpoints. It has been previously indicated that in low carbon steels containing 12 to 14 per cent chromium, up to about 0.10 per cent nitrogen has a pronounced

effect on physical properties. Such steels are commonly known as the rustless iron type and are employed in many applications that require certain engineering characteristics with appreciable resistance to corrosion. The marked effect of nitrogen in increasing the hardening ability of these steels without seriously decreasing their ductility or toughness is most clearly illustrated by the results of tests given in Table I. It is shown in this table that a wrought 13 per cent chromium steel containing 0.08 per cent nitrogen and 0.07 per cent carbon is easily hardened to yield a Brinell number of about 400 and also that tempering the hardened steel at 600 degrees Cent. (1110 degrees Fahr.) imparts to the metal an ultimate strength of 123,500 pounds per square inch, a yield point of 106,500 pounds per square inch and an elongation in two inches of 21 per cent with a reduction in area of 65 per cent. This hardened and tempered high nitrogen 13 per cent chromium steel also exhibited an Izod impact value of 60 foot-pounds. The ability to secure economically such remarkable physical characteristics in steels of this type provides a corrosion-resisting metal of many possibilities. Usually to procure such properties it is necessary to introduce into these low chromium steels small proportions of other metallic elements, and it is noteworthy to observe that nitrogen appears to function similarly in this group of steels. It is nevertheless advisable to state that if the object is to secure optimum softness in the 12 to 14 per cent chromium steels, it is unwise to introduce nitrogen, as the experience has been that this element serves most effectively in the opposite manner.

There is a difference of opinion at present concerning the toughness of the low carbon 16 to 18 per cent chromium steels. The general opinion is that unless these steels are treated with a special agent or are fabricated under exacting conditions their toughness as determined by impact tests is fairly low. While confirmation can not be accorded this belief, the toughness exhibited by high nitrogen, low carbon 16 to 18 per cent chromium steels is at least enlightening. Even moderate percentages of nitrogen serve to refine the grain structure of these steels and assure metal of appreciable toughness. The data given in Table II reveal that impact values of the order of 60 to 80 ft-lbs. are obtainable in the fully annealed low carbon-high nitrogen 16 to 18 per cent chromium steels. An explanation for these relatively high impact values may be based on the previously described heating and cooling curve which indicates that the chromium nitrides are quite soluble in the high chromium steel, permit-

Table II

Physical Tests on Wrought High and Low Nitrogen Steels Containing 16-18 Per Cent Chromium

Standard Samples Taken from 1-Inch Round Bars

Per Cent Cr*	Per Cent C	Per Cent N	Condition of Metal	Yield Point Lbs. Per Sq. Inch	Max. Stress	Per Cent Elongation in 2 Inches	Per Cent Reduction of Area	Izod Impact Ft.-Lb.	Brinell Hardness
16.25	0.10	0.03	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	42,000	72,000	30	56	60	137
17.28	0.10	0.031	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	47,000	77,000	28	56	48	140
17.95	0.07	0.032	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	44,700	72,000	29	60	42	140
16.39	0.07	0.12	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	61,000	92,000	27	66	86	183
17.23	0.06	0.11	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	63,000	94,500	27	61	62	179
18.46	0.08	0.17	Held 3 hours at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	68,000	103,000	25	57	61	174

*These steels also contain normal percentages of silicon and manganese.

ting the formation of austenite[4] that decomposes into the various constituents on cooling, and the final result is to impart to these steels properties similar to those of the low carbon 12 to 14 per cent chromium type, a metal of unquestioned toughness.

The effects of nitrogen on the wrought steels containing 20 per cent or more of chromium will now be discussed. The ease with which large grains develop in low carbon steels of this class is well-known amongst those familiar with the manufacture of such steels. The presence of these large grains has caused appreciable difficulties in fabricating the steels by bending, forming, cold drawing or otherwise shaping the material to meet a given requirement. While the addition of nitrogen must not be considered a panacea, its presence has rendered the steels far more suitable for these operations, and it is the belief that the improvement has been brought about by the high solubility of the nitrides in chromium ferrite, which as will be shown later acts to limit grain-size materially. The nitrogen appears to be so influential in this respect that little trouble should be had in securing fine-grained hot-rolled steels.

The results of tests conducted on commercially rolled high

[4] "Alloys of Iron and Chromium," by V. N. Krivobok, TRANSACTIONS, American Society for Metals, Vol. XXIII, June 1935.

Table III

Physical Tests on High and Low Nitrogen Steels Containing 25 Per Cent Chromium

Samples Taken from Commercially Rolled $\frac{3}{16}$ Inch and ¼ Inch Plate

Per Cent Cr†	Per Cent C	Per Cent N	Condition of Metal	Yield Point Lbs. Per Sq. Inch	Max. Stress Lbs. Per Sq. Inch	Per Cent Elongation in 2 Inches	Brinell Hardness
*							
26.19	0.15	0.07	As hot-rolled	52,600	79,300	16	174
26.19	0.15	0.07	Heated at 875 degrees Cent. (1605 degrees Fahr.) 8 hours and water-quenched.	53,250	76,500	34	159
26.19	0.15	0.07	Heated at 950 degrees Cent. (1740 degrees Fahr.) ½ hour and air-cooled.	46,800	69,900	6	159
26.19	0.15	0.07	Heated at 1050 degrees Cent. (1920 degrees Fahr.) ½ hour and air-cooled.	58,300	67,700	3	166
26.19	0.15	0.07	Heated at 1150 degrees Cent. (2100 degrees Fahr.) 15 minutes and water-quenched.	72,000	80,800	2	207
*							
25.30	0.19	0.24	As hot-rolled	79,200	112,700	18	223
25.30	0.19	0.24	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and water-quenched.	58,100	87,500	25	183
25.30	0.19	0.24	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and air-cooled.	60,750	88,000	27	183
25.30	0.19	0.24	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and furnace-cooled.	62,900	91,600	24	212
**							
25.08	0.15	0.22	As hot-rolled	83,000	98,300	18	217
25.08	0.15	0.22	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and water-quenched.	50,800	78,150	31	166
25.08	0.15	0.22	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and air-cooled.	50,250	78,150	31	166
25.08	0.15	0.22	Heated at 925 degrees Cent. (1700 degrees Fahr.) ½ hour and water-quenched.	50,800	79,200	29	170
**							
25.08	0.15	0.22	Heated at 950 degrees Cent. (1740 degrees Fahr.) ½ hour and air-cooled.	53,000	78,400	33	179
25.08	0.15	0.22	Heated at 1050 degrees Cent. (1920 degrees Fahr.) ½ hour and air-cooled.	52,400	77,300	34	174
25.08	0.15	0.22	Heated at 1150 degrees Cent. (2100 degrees Fahr.) 15 minutes and water-quenched.	81,100	105,600	38	217

*¼ in. plate.

**$\frac{3}{16}$ in. plate

†These steels contain normal percentages of silicon and manganese.

nitrogen 25 per cent chromium steel plate obtained from two sources are given in Table III. The samples were tested in the hot-rolled condition and after heating for various periods at temperatures extending from about 875 to 1150 degrees Cent. (1605-2100 degrees Fahr.). In some instances the samples were water-quenched

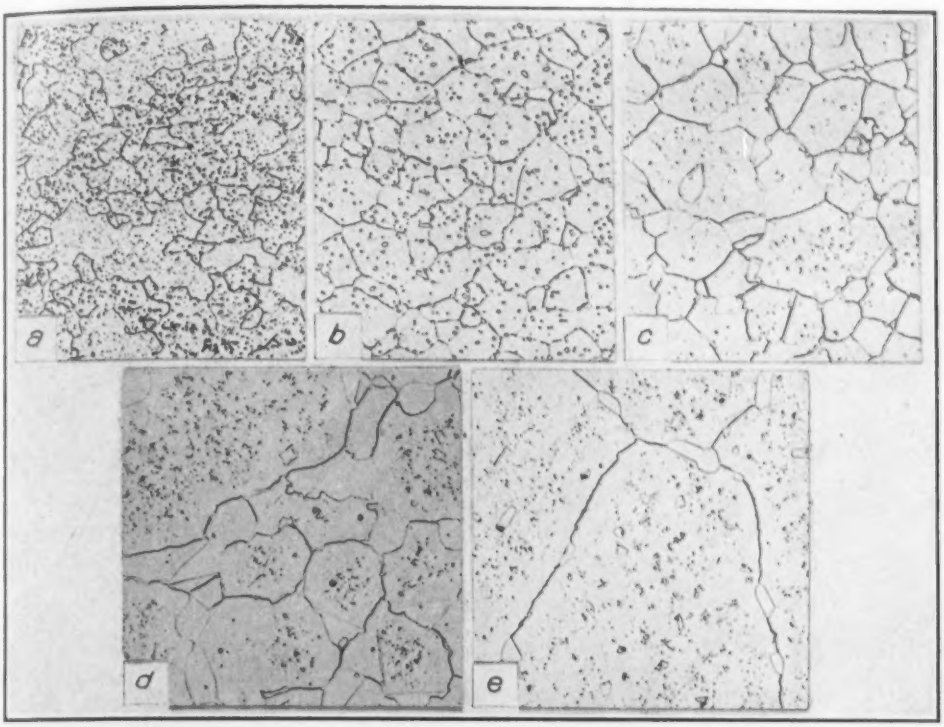


Fig. 3—Effect of Heating at Different Temperatures on the Structure of the Low Nitrogen 25 Per Cent Chromium Steels. a—25.50 Per Cent Chromium, 0.14 Per Cent Carbon and 0.05 Per Cent Nitrogen Steel Annealed 8 Hours at 875 Degrees Cent. and Water-Quenched. × 100. b—Same Steel Annealed as Above. Held 2 Hours at 1050 Degrees Cent. (1920 Degrees Fahr.) and Air-Cooled. × 100. c—Same Steel Annealed as Above. Held 2 Hours at 1100 Degrees Cent. (2010 Degrees Fahr.) and Air-Cooled. × 100. d—Same Steel Annealed as Above. Held 2 Hours at 1150 Degrees Cent. (2100 Degrees Fahr.) and Air-Cooled. × 100. e—Same Steel Annealed as Above. Held 7 Days at 1100 Degrees Cent. (2010 Degrees Fahr.) and Air-Cooled. × 100.

while in others they were air-cooled or furnace-cooled. These results reveal that there is a relatively wide range of temperature in which the high nitrogen 25 per cent chromium steels can be annealed to impart what is considered good ductility for a steel of this type. It is generally accepted that the low nitrogen 25 per cent chromium steels should be quenched from the annealing temperature to avoid the brittleness that develops so rapidly on exposure within the temperature range between 600 and 400 degrees Cent. (1110-750 degrees Fahr.). The present results show that high nitrogen steels of similar chromium content may be even furnace-cooled from the annealing temperature without seriously impairing ductility although this method of cooling is not recommended. It is further enlightening to note that the high nitrogen steels can be softened in a relatively short period at 925-1000 degrees Cent. (1700-1830 degrees

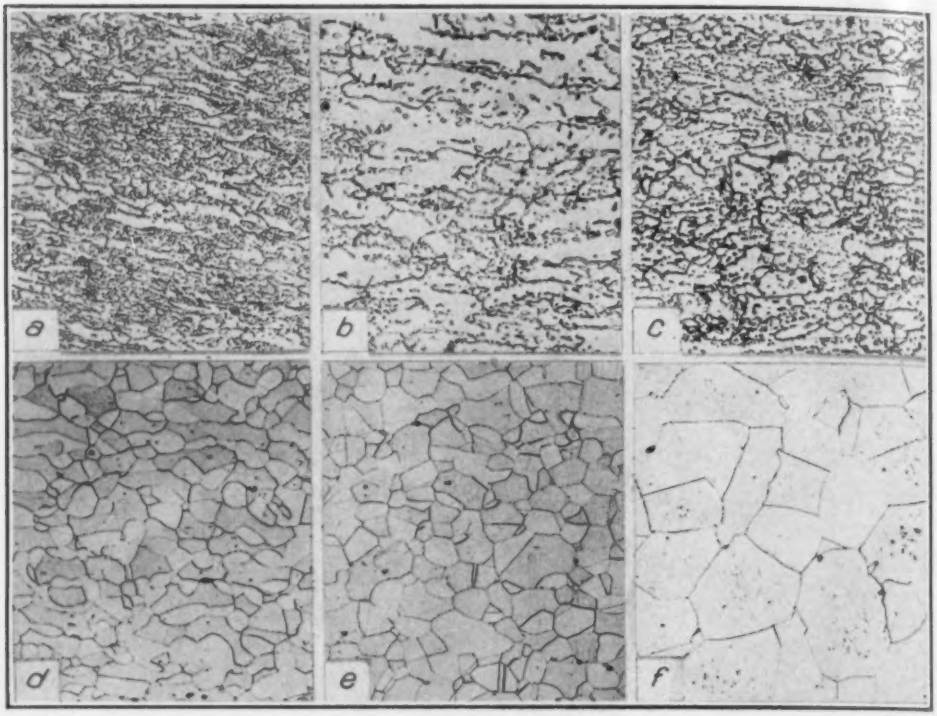


Fig. 4—Effect of Heating at Different Temperatures on the Structure of the High Nitrogen 25 Per Cent Chromium Steels. a—25.05 Per Cent Chromium, 0.15 Per Cent Carbon, and 0.22 Per Cent Nitrogen Steel Annealed 4 Hours at 875 Degrees Cent. (1605 Degrees Fahr.) and Air-Cooled. × 100. b—Same Steel Annealed as Above. × 250. c—Same Steel Annealed as Above. Held 2 Hours at 1050 Degrees Cent. (1920 Degrees Fahr.) and Air-Cooled. × 100. d—Same Steel Annealed as Above. Held 2 Hours at 1100 Degrees Cent. (2010 Degrees Fahr.) and Air-Cooled. × 100. e—Same Steel Annealed as Above. Held 2 Hours at 1150 Degrees Cent. (2100 Degrees Fahr.) and Air-Cooled. × 100. f—Same Steel Annealed as Above. Held 7 Days at 1100 Degrees Cent. (2010 Degrees Fahr.) and Air-Cooled. × 100.

Fahr.), while a short exposure to 1150 degrees Cent. (2100 degrees Fahr.) fails to cause a serious loss of ductility. As a matter of fact the steel was equally as ductile after exposure to this latter temperature, and possessed remarkable strength as indicated by the maximum stress and yield point values.

These results were quite unexpected in view of previous experience with the normally low nitrogen 25 per cent chromium steels. It thus became advisable to ascertain what happened when the high and normally low nitrogen steels were subjected for relatively short and long periods to high temperatures. The study of the steels in this respect demanded that samples be held at various temperatures for investigation. The photomicrographs of Figs. 3 and 4 provide ample data that explain the difference in the behavior of the respective steels at high temperatures. Fig. 3 shows the structures of ¼-

Table IV

Physical Tests on High and Low Nitrogen 25 Per Cent Chromium Steels After Treatment at Elevated Temperatures

Standard Samples Taken from Commercially Rolled Plate

Per Cent Cr†	Per Cent C	Per Cent N	Condition of Metal	Yield Point Lbs. Per Sq. Inch	Max. Stress Lbs. Per Sq. Inch	Per Cent Elongation in 2 Inches
*						
25.50	0.14	0.05	Heated at 875 degrees Cent. (1605 degrees Fahr.) 8 hours and water-quenched.	54,350	75,600	35
25.50	0.14	0.05	Heated at 875 degrees Cent. (1605 degrees Fahr.) 8 hours and water-quenched. Held 7 days at 1100 degrees Cent. (2010 degrees Fahr.) and air-cooled.	None shown	39,100	0
**						
25.08	0.15	0.22	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and air-cooled.	50,250	78,150	31
25.08	0.15	0.22	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and air-cooled. Held 7 days at 1100 degrees Cent. (2010 degrees Fahr.) and air-cooled.	58,250	83,600	34

*¼ inch plate.

**⅜ inch plate.

†The steels also contain normal percentages of silicon and manganese.

inch commercially made low nitrogen 25 per cent chromium steel plate after treatment for varying periods at temperatures between 875 and 1150 degrees Cent. (1605-2100 degrees Fahr.). Examination of these photographs shows that in the annealed condition (a) the 25 per cent chromium steel consists of relatively small grains which become somewhat enlarged on exposure for only two hours at 1050 degrees Cent. (1920 degrees Fahr.), while as a result of the treatments at 1100 and 1150 degrees Cent. (2010-2100 degrees Fahr.) the increase in grain-size may be considered abnormal. It is also revealed that holding the normally low nitrogen steel for 7 days at temperatures in the neighborhood of 1100 degrees Cent. (2010 degrees Fahr.) produces a grain of sufficient size to occupy the entire field of the attached photograph. Attention is now directed to Fig. 4 in which is shown the effect of heating to the same temperatures on the structure of commercially produced ¼-inch plate of a high nitrogen 25 per cent chromium steel. This steel is composed of remarkably fine grains in the annealed condition (a and b) while exposure for two hours at temperatures of 1050, 1100 and 1150 degrees Cent. (1920, 2010, 2100 degrees Fahr.) fails to produce a marked increase in grain-size. It is further shown that holding this steel for 7 days at 1100 degrees Cent. (2010 degrees Fahr.) produces only a minor increase in grain-size.

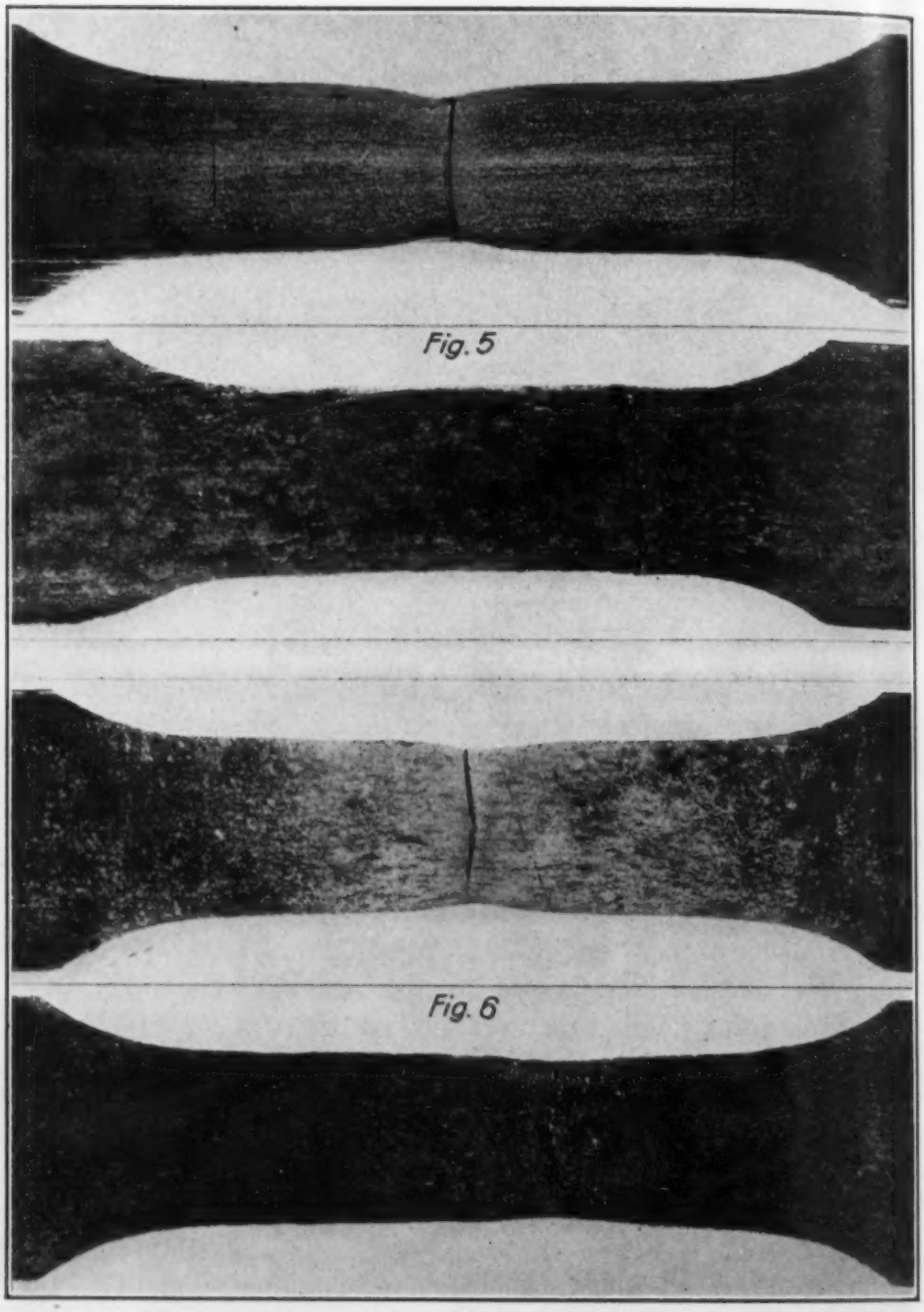


Fig. 5

Fig. 6

Fig. 5—Effect of Continued Holding at 1100 Degrees Cent. (2010 Degrees Fahr.) on the Physical Characteristics of a Low Nitrogen 25 Per Cent Chromium Steel. Top—Ductility of Annealed ¾-Inch Plate of 25.50 Chromium, 0.14 Carbon and 0.05 Nitrogen. Bottom—Same Steel Held 7 Days at 1100 Degrees Cent. Air Cooled. Tested at Room Temperature.

Fig. 6—Effect of Continued Holding at 1100 Degrees Cent. (2010 Degrees Fahr.) on the Physical Characteristics of a High Nitrogen 25 Per Cent Chromium Steel. Top—Ductility of Annealed ¾-Inch Plate of 25.08 Chromium, 0.15 Carbon and 0.22 Nitrogen. Bottom—Same Steel Held 7 Days at 1100 Degrees Cent. Tested at Room Temperature.

The fact that the high nitrogen 25 per cent chromium steels possess improved resistance to grain growth at elevated temperatures is fully confirmed by the data given in Table IV and the illustrations in Figs. 5, 6, 7, and 8. The data in Table IV pertain to high and low nitrogen steel samples held for 7 days at 1100 degrees Cent. (2010 degrees Fahr.) followed by testing in tension, while Figs.

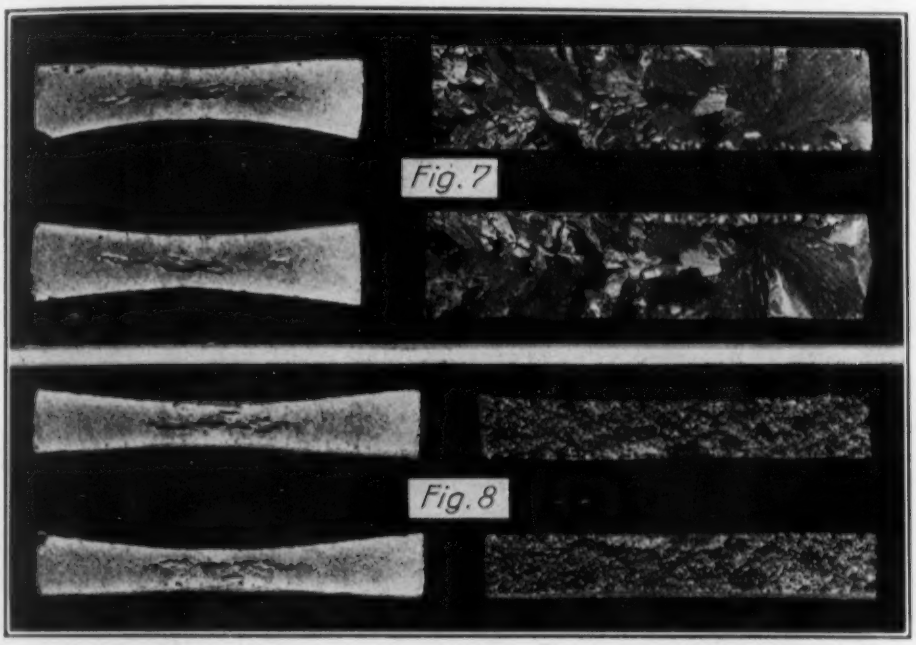


Fig. 7—These Photographs Illustrate the Fractured Ends of the Tensile Samples Shown in Fig. 5. The Fractures on the Left Are Those of the Annealed Plate, While Those on the Right Represent the Plate Held at 1100 Degrees Cent. for 7 Days. The Photograph Shows the Tremendous Grain Growth that Occurred in the Low Nitrogen 25 Per Cent Chromium Steel at 1100 Degrees Cent. This Undoubtedly Accounts for the Brittleness Exhibited by the Steel. × 2.

Fig. 8—These Photographs Show the Broken Ends of the Tensile Samples Described in Fig. 6. The Fractures on the Left Are Those of the High Nitrogen Steel in the Annealed Condition, While Those on the Right Represent the Same Steel After Treatment at 1100 Degrees Cent. for 7 Days. It Is Evident That Very Little Grain Growth Took Place During the Exposure to This Temperature. × 2.

5, 6, 7, and 8 depict the appearance of the samples after the tensile test. As shown in this table, the steel of normal nitrogen content is quite ductile in the annealed state, and when tested in this condition exhibits a silky fracture. After holding at 1100 degrees Cent. (2010 degrees Fahr.) this steel fractured without elongating to a measurable extent under a load less than that representing the yield point of the metal in the fully annealed condition. The explanation of this result is undoubtedly found in a study of Fig. 7 which reveals that the grains of the steel had increased to a size almost equivalent to the

thickness of the plate. The results secured with the high nitrogen 25 per cent chromium steel were quite different, as this steel suffered no decrease in ductility or strength resulting from the 7-day exposure

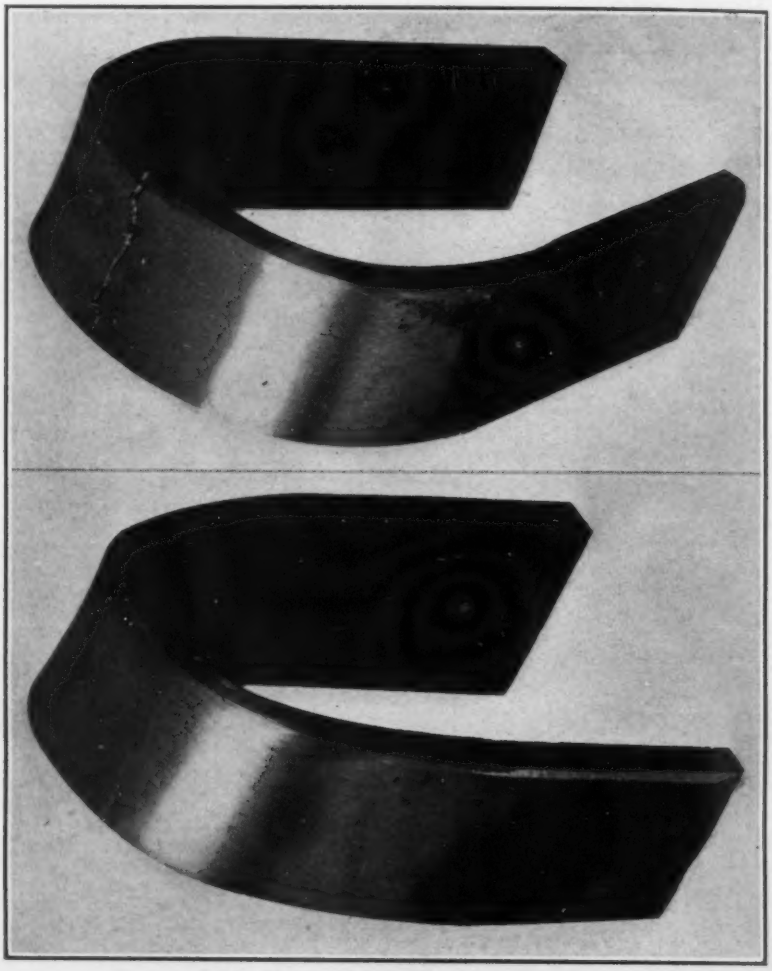


Fig. 9—The Top Photograph Shows the Results of a Bend Test on a Weld Made by the Oxyacetylene Process in ¼-Inch Plate of a Steel Containing 25.30 Per Cent Chromium, 0.19 Per Cent Carbon and 0.24 Per Cent Nitrogen. The Lower Photograph Reveals the Condition of an Arc Weld in the Same Plate After Bending. It Will Be Observed that Both Welds Exhibited Some Ductility, Especially in the Zones Adjacent to the Welds.

to the same temperature, and as shown in Fig. 8 only a slight increase in grain-size took place.

It is hardly a questionable fact that the high nitrogen steel performed remarkably well under the conditions of this test. Referring to the photomicrographs given in Fig. 4, it may be observed that in

Table V

Physical Tests on Welds Made in Nitrogen-Bearing 25 Per Cent Chromium Steels

Standard Samples Machined from Welds Made in Annealed* ¼ Inch Plate

Per Cent Cr†	Per Cent C	Per Cent N	Method of Welding	Condition of Weld	Yield Point Lbs. Per Sq. Inch	Max. Stress Lbs. Per Sq. Inch	Per Cent Elongation in 1 Inch
24.19	0.17	0.24	Oxyacetylene	As welded.	66,500	92,700	3
24.19	0.17	0.24	Oxyacetylene	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and air-cooled.	57,100	80,500	7
25.30	0.19	0.24	Arc	As welded.	64,000	85,500	7
25.30	0.19	0.24	Arc	Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and air-cooled.	53,600	82,400	10

* Heated at 875 degrees Cent. (1605 degrees Fahr.) 4 hours and air-cooled.
†The steels also contain normal percentages of silicon and manganese.

the course of heating the high nitrogen steels to high temperatures a constituent develops which is of the austenitic type, and there are appreciable quantities of this constituent in the structure of the high nitrogen steels. It is probable that this constituent produces a keying action that greatly retards the tendency for the grains to enlarge on heating.

Little difficulty is met with in welding the 25 per cent chromium steels containing nitrogen with rods of the same analysis, and practically all the nitrogen is recovered in the weld metal. As shown in Fig. 9 the welds obtained can be deformed appreciably in the welded zone and in the sections adjacent to the welds before failure occurs, another good indication of the improved fabricating properties possessed by the high nitrogen steels. The results of tensile tests conducted on welds made in ¼-inch plate are given in Table V. These experiments show that in the unannealed condition welds made in the high nitrogen 25 per cent chromium steels possess some ductility, while annealing greatly improves this property. It is probable that the excellent strength exhibited by these welds is due to the comparatively fine grains constituting the weld metal and the metal adjacent to the welds.

It is interesting to report that the high nitrogen 25 per cent chromium steels can be fabricated into seamless tubes of good quality, and the procedure to be employed is little different from that used ordinarily on the normally low nitrogen steels. The hot-rolled, annealed, and descaled high nitrogen-chromium steel seamless tubing can be readily cold drawn to smaller diameters without fear of frac-

turing the metal. The product obtained after this operation is of an excellent quality as shown in Fig. 10, which illustrates the results of a bend test made on a section of a cold drawn and annealed tube of this steel. After heating for 4 hours at 875 degrees Cent. (1605 degrees Fahr.) and air cooling, a sample of the same tubing which had an outside diameter of 2 inches with a 1/8-inch wall thickness,

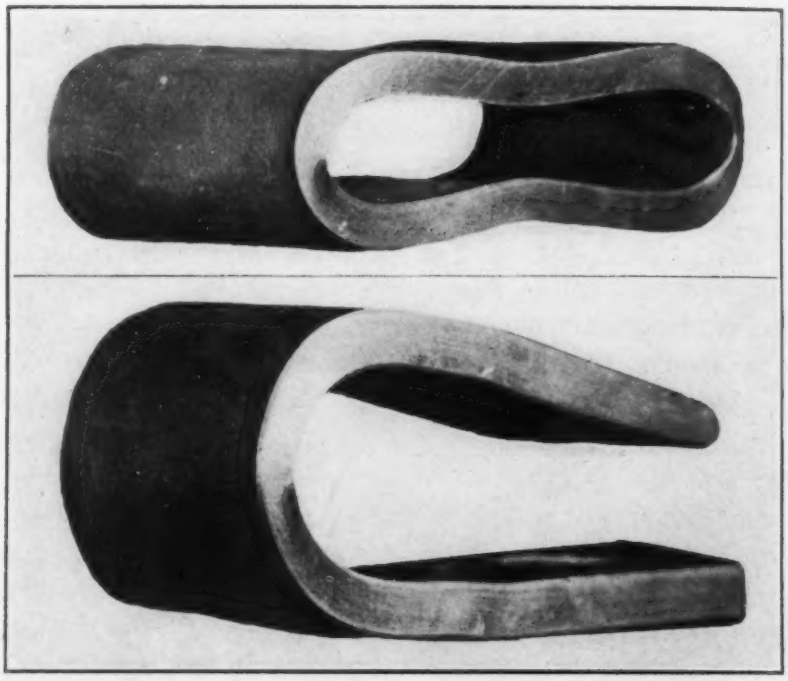


Fig. 10—Upper—Sample of a Cold Drawn and Annealed Seamless Tube of a Steel Containing 24.19 Per Cent Chromium, 0.17 Per Cent Carbon and 0.26 Per Cent Nitrogen. No Signs of Failure Could Be Detected During the Bend Test on This Sample. Lower Picture is of a Hot-Rolled Plate of an Unannealed Steel Containing 25.08 Per Cent Chromium, 0.15 Per Cent Carbon and 0.22 Per Cent Nitrogen. Possesses Appreciable Ductility.

gave a yield point of 56,500 pounds per square inch, a maximum stress of 86,100 pounds per square inch, and elongation of 32 per cent in 2 inches, demonstrating fully the excellent quality of the cold drawn metal.

The opportunity is now presented to describe the effects of introducing into the high nitrogen steels containing in the vicinity of 22 and 25 per cent chromium, small amounts of the elements nickel and copper. It has been previously pointed out that on heating to the proper temperatures the chromium nitride employed in introducing nitrogen into these steels goes into solution, forming goodly quan-

tities of an austenitic constituent. It was thus predicted that if small additions of other austenite-forming elements were incorporated a further enhancement of toughness might be obtained. The physical data given in Table VI concern high nitrogen 22 and 25 per cent chromium steels with and without additions of these metallic elements. The data show first that the high nitrogen 22 and 25 per cent chromium steels are comparatively tough for metal so high in chromium. These steels also possess considerable ductility and are relatively soft. The enhancement in toughness imparted to similar high nitrogen steels by small percentages of copper or nickel is evident, although other data reveal that in the absence of nitrogen the effect of either element is not so pronounced.

The data herein presented leave little doubt concerning the pronounced effects of alloyed nitrogen on the physical characteristics of high chromium steels, and it must be stated that the utility of nitrogen can be realized only in chromium steels of high quality. A goodly part of this discussion has been purposely directed to the effects of nitrogen on the properties of the wrought low carbon-high chromium steels, because in a previous communication stress was laid on cast steels of this type.

A resumé of these data reveals that the high solubility of chromium nitrides in chromium iron greatly enhances the hardening capacity of the 12 to 14 per cent chromium steels without detrimentally affecting other valuable characteristics, while in steels containing 16 to 18 per cent chromium or slightly higher the presence of nitrogen seems to assure metal of appreciable toughness. Nevertheless, the hardening ability of the 16 to 18 per cent chromium steels is also increased by a proper control of nitrogen content. The 12 to 14 per cent chromium steels should contain 0.06 to 0.10 per cent nitrogen to secure optimum results, and in the 16 to 18 per cent chromium steels the nitrogen content should be between about 0.08 and 0.16 per cent.

The influence of 0.15 to 0.25 per cent nitrogen in producing fine-grained steels containing 20 to 25 per cent chromium with improved toughness and remarkable resistance to deterioration at elevated temperatures has been fully demonstrated. There are probably several explanations that may be given for the marked effects of nitrogen on the properties of the high chromium steels, but the belief is held that these effects are due primarily to the solubility of chromium nitride in chromium iron solid solution on exposure to

Table VI

Physical Tests on Wrought High Nitrogen 22 and 25 Per Cent Chromium Steels Containing Copper and Nickel

Standard Samples Taken from 1-Inch Round Bars

Per Cent					Condition of Metal	Yield Point Lbs. Per	Max. Stress Sq. Inch 2	Per Cent Elongation in Inches	Per Cent Reduction of Area	Izod Impact Ft.-Lb.	Brinell Hardness
Cr*	C	N	Cu	Ni							
22.46	0.08	0.032	...	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 8 hours and water-quenched.	46,500	77,600	30	60	4	149
22.30	0.10	0.21	...	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and water-quenched.	54,000	85,000	29	66	24	166
22.30	0.10	0.21	...	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and air-cooled.	54,500	85,500	27	61	18	166
22.73	0.10	0.25	0.53	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and water-quenched.	53,000	88,500	26	56	30	166
22.73	0.10	0.25	0.53	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and air-cooled.	57,100	89,800	27	55	20	156
22.52	0.10	0.26	1.04	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and water-quenched.	54,000	87,800	27	57	25	174
22.52	0.10	0.26	1.04	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and air-cooled.	69,000	95,500	26	56	22	174
22.27	0.12	0.26	...	1.20	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and water-quenched.	67,000	124,000	23	47	37	183
22.27	0.12	0.26	...	1.20	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and air-cooled.	70,000	120,000	22	44	28	183
26.20	0.14	0.045	...	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 8 hours and water-quenched.	56,000	83,000	26	51	2	156
25.66	0.12	0.30	...	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and water-quenched.	54,000	85,500	30	60	13	179
25.66	0.12	0.30	...	...	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and air-cooled.	59,500	88,500	29	61	8	174

Table VI (Continued)

Per Cent						Yield Point Lbs. Per Sq. Inch	Max. Stress	Per Cent Elongation in 2 Inches	Per Cent Reduction of Area	Izod Impact Ft.-Lb.	Brinell Hardness
Cr*	C	N	Cu	Ni							
25.09	0.10	0.29	...	1.56	Heated at 900 degrees Cent. (1650 degrees Fahr.) 6 hours and water-quenched.	62,000	94,000	25	50	37	183

*The steels contain normal percentages of silicon and manganese.

elevated temperatures. In this respect these nitrides appear to function in the chromium steels quite similarly to carbides in ordinary steels.

Precaution must be exercised in making claims regarding the influence of nitrogen on the corrosion resistance of the various high chromium steels, although it must be appreciated that the steels have been thoroughly investigated in this respect. The indications are that nitrogen does not seriously affect this property of the steels. However, it is recognized that the results of the well-known tests that are applied to the high chromium steels should be interpreted with caution, especially when the object in mind has to do with practical application. Experience with the chromium steels has taught that their value can be based only on service. Despite the fact that nitrogen has imparted such a pronounced improvement, it is felt that the steels to which this element has been added should be considered in like manner so that the utility of the nitrogen addition may serve industry to the utmost.

The efforts of Cecil Chadwick, F. E. Bacon and James Thompson in assisting generally in making and testing the steels should be especially commented upon, as should the assistance given by W. L. Harbrecht in producing the large ingots investigated.

DISCUSSION

Written Discussion: By E. C. Wright, metallurgist, National Tube Co., Ellwood City, Pa.

We have read with considerable interest Mr. Franks' paper describing the chromium-nitrogen steels, as we have encountered at least one industrial application of these low carbon-chromium-nitrogen alloys and have fabricated two lots of the higher chromium alloy into commercial equipment. The advantages which Mr. Franks' paper points out in reference to the improved

ductility and resistance to grain growth of these nitrogen-bearing chromium alloys have also been completely verified in our experience. The alloy with which we are familiar contains approximately 25 per cent chromium, 0.12 per cent carbon, and 0.25 per cent nitrogen. Alloy of this composition was made into seamless tubing which was later fabricated into a coil containing about 125 feet of tubing. This required middle welding of short length tubing prior to coiling, and several coils have been successfully fabricated from this special analysis. An alloy was desired which contained no nickel and the extreme difficulty in making such equipment from plain chromium alloys of the 25 per cent composition made the development of equipment highly questionable.

The 25 per cent chromium-nitrogen-bearing alloy was found to have much better forging characteristics than the plain chromium alloy of similar chromium content. It is well known that the low carbon 25 per cent chromium alloys must be finish forged or rolled at a low temperature, certainly below 1600 degrees Fahr. (870 degrees Cent.) or extremely coarse grain structures are likely to be encountered. When the 25 per cent chromium alloy reaches this structural state it is practically worthless, since the coarse grain cannot be altered by any heat treatment, and only by further working. The 25 per cent chromium alloys containing approximately 0.20 per cent nitrogen do not have this tendency for high temperature grain growth and consequently can be forged with a wide range of finishing temperatures without developing coarse brittle structures.

It was found that 25 per cent chromium alloys containing nitrogen were much superior in every way to the plain 25 per cent chromium alloys in responding to cold work. The 25 per cent chromium-nitrogen tubing could be cold drawn with much greater ease than the alloy not containing nitrogen and it also responded to heat treatment after drawing much more uniformly.

Probably the greatest advantage noticed in connection with the high chromium-nitrogen alloy was the greater ease of welding and superior ductility after welding. It is well known that the welding of plain 25 per cent chromium alloys leads to very unsatisfactory results due to the extreme coarse crystallization of the metal at the zone of fusion which cannot be remedied after welding. Test welds made on the 25 per cent chromium with nitrogen metal using coated "18-8" rods for arc welding, developed a full strength metal with high ductility; similar results were obtained with atomic hydrogen welding wherein the 25 per cent chromium-nitrogen metal was used as an uncoated rod. Neither of these welds has developed any coarse crystal structure adjacent to the weld, and both have shown full ductility and tensile strength. This feature is also well brought out in the discussion of welds in Mr. Franks' paper.

Resistance of the 25 per cent chromium-nitrogen alloys to oxidation is also extremely good up to temperatures as high as 2000 degrees Fahr. (1095 degrees Cent.) and they compare favorably with the plain 25 per cent chromium alloys in this respect.

Written Discussion: By H. D. Newell, chief metallurgist, Babcock and Wilcox Tube Co., Beaver Falls, Pa.

Mr. Franks' interesting paper on the influence of nitrogen on high chromium steels or irons suggests that more reliable heat resisting alloys may be

the result. This is accomplished by incorporating a gaseous element which has heretofore been considered detrimental.

Nitrogen forms compounds with iron similar in many respects to iron-carbon compounds and the iron-nitrogen diagram is not greatly different from the iron-carbon one except as to concentration. This should be borne in mind where nitrogen is employed for its specific action.

The grain-growth inhibiting action of nitrogen in both plain ferritic chromium alloys and in austenitic chromium-nickel alloys has been confirmed by the writer. This was done by means of trial induction furnace melts cast into 4-inch square tapered ingots. These nitrogen-containing ingots had a much smaller grain-size than similar compositions without added nitrogen. Greater latitude in temperature working ranges is thereby gained especially in the plain high chromium materials without danger of detrimental effects such as poor surface, low ductility and poor impact value due to coarsened grain structure.

These benefits are especially noticeable in cold drawing operations where much trouble is encountered in breakage in starting the large-grained ferritic alloys. Ferritic chromium-iron alloys in the large-grained condition are quite tender and must be handled very carefully until sufficient mechanical work has been done to break down the grain-size and elongate or fiber the crystals. Warming on the initial passes is helpful to restore some toughness to the metal.

Mr. Franks refers to the fabrication of high nitrogen 25 per cent chromium steel into seamless tubes. In connection with cold drawing the high nitrogen alloys, it is well to keep in mind that too great an excess of nitrogen interferes with cold working and may more than offset the benefits gained through reduction of grain-size. In certain experimental melts, it was observed that considerable hardness and stiffness were encountered in tube drawing when the alloys contained 0.30 to 0.34 per cent nitrogen. In commercial lots, the workability and resistance to grain-growth are substantially improved by a nitrogen content of approximately 0.20 per cent.

It has been observed that nitrogen additions improve the life of cast alloys and welded overlays required to withstand combined heat and abrasive action. In this field, nitrogen-bearing alloys should find an increasing field of usefulness. The procedure of obtaining nitrogen by use of high nitrogen ferrochromium does not alter usual melting or casting practice although unsound castings may result from efforts to add a maximum nitrogen content.

Putting an "evil-doer" to work such as Mr. Franks has done with nitrogen constitutes a real metallurgical advance.

Written Discussion: By V. N. Krivobok, Allegheny Steel Co., Brackenridge, Pa.

I have always held that a discussion of my colleagues' work should be an attempt to offer helpful suggestions; such suggestions may pertain to interpretation of results or may contain different but justifiable and logical explanation of observed phenomena.

A discussion of this nature can be attempted only when the discusser agrees with the basic facts and experimental findings: then the discussion becomes a pleasant interchange of ideas, and since the findings of my associates and myself are quite in agreement with those of Mr. Franks, it is with sincere

pleasure that I am undertaking my individual interpretation and evaluation of the facts contained in the valuable contribution before us.

My opening suggestion is that Mr. Franks' statement regarding the influence of nitrogen on the constitution of chromium alloys may be misinterpreted. While on this subject, he writes that we have "a number of good indications," —to quote him—"that nitride promotes austenite formation." I do not think we are ready to evaluate the role of nitrides. The definitely established fact is that the ternary system iron-chromium-nitrogen contains several fields within which austenite (iron-chromium-nitrogen solid solution closely resembling austenite) will be found, within certain limits of concentrations and temperatures, in equilibrium with one or two other phases. The proof, in the form of metallographic study and dilatometric observations, will be found in the present paper of the author as well as in other previous publications.[1] This austenite behaves much like the similar constituent of plain carbon steels and is responsible for the properties and characteristics of nitrogen-bearing iron-chromium alloys. It is stable only at elevated temperatures and consequently is readily subjected to decomposition, the results of which depend upon the rate at which such decomposition is allowed to proceed. In this connection, it should be desirable to offer further discussion of the dilatometric curves. I cannot accept a statement that solution of nitrides takes place on heating at 904 degrees Cent. (1660 degrees Fahr.) and, reversely, on cooling, precipitation starts at 846 degrees Cent. (1555 degrees Fahr.). In the first place, I believe that the process detected by the dilatometer is that of austenite formation with perhaps subsequent solution of nitrides. Phenomena of this type depend so much on the rate of heating and cooling that it is unwise to assign to it a definite temperature unless of course it has been ascertained that the transformation had occurred at stated temperature as demanded by the conditions of equilibrium. In our work—to clarify this point—we found that the transformation could be made to occur, at will, at almost any temperature. And I further believe that the results of this transformation modify the properties much more readily than the grain-size. About this, I shall speak later.

I do not think that one would find it easy to justify the statement regarding the necessity of maintaining a certain relationship—nitrogen to chromium—and especially the actual figures. The amount of nitrogen present should depend on the properties desired. The relationship can only be established when we know the type of combination existing between iron, chromium or nitrogen, the limits of solubility at various temperatures, etc. Such data are, as yet, not available. Without them, we can evaluate only approximately or shall I say speculate upon the influence and the full benefits of variable nitrogen concentrations.

As I read on, I come to the statement that nitrogen has a pronounced effect on physical properties. The care with which Mr. Franks conducts his work is so well known that it may appear unjustifiably superfluous to exclaim "Yes, indeed." I have a definite reason for doing so: I do not agree with a general statement further down that hardened and tempered high nitrogen 13 per cent chromium steel exhibits an Izod impact value of 60 foot-pounds. It

[1] V. N. Krivobok, "Alloys of Iron and Chromium," Campbell Memorial Lecture, October, 1934, published in TRANSACTIONS, American Society for Metals, March, 1935, Vol. 23, p. 1.

may or it may not. One must not have the idea that such values are characteristic of all quenched and tempered chromium-nitrogen steels regardless of the temperature of treatment. As a matter of fact, hardening and tempering within some temperature ranges may very successfully be used to separate low and high nitrogen alloys: high nitrogen alloys will be found relatively more brittle than the low nitrogen alloys. Further, I should like to modify the statement which reads that even moderate percentages of nitrogen added to steels of 16-18 per cent chromium assure the metal of appreciable toughness. I feel certain that Mr. Franks means "after proper heat treatment." I am very much interested in the question of nitrogen additions to steels. I believe that definite and valuable improvements may be thus secured. For this reason alone, I am anxious not to have Mr. Franks misunderstood by those who possess a less thorough knowledge of the subject than he.

And while we are discussing toughness, or rather, while I continue reading the paper, I see on page 974 a statement which I interpret to mean that in order to obtain fair toughness in alloys of from 16-18 per cent chromium, rather exact conditions of treatment are necessary. I would like to suggest further that there is a critical composition at approximately 16.5 per cent chromium. When this chromium concentration is exceeded the toughness of the alloys, in my opinion, is not only the question of careful treatment, but also careful fabrication, including melting practice. I say all this for the purpose of emphasizing the importance of nitrogen as an addition.

The interesting data pertaining to the metallographic study and to the type of fractures in tensile tests deserve careful study. I indeed concur in the expressed opinion of Mr. Franks that additions of nitrogen have a very definite effect on the grain-size. One may question, however, the emphasis laid on this observation. To quote "After holding at 1100 degrees Cent. (2010 degrees Fahr.), the steel with lower nitrogen fractured without elongating to a maximum extent under a load less than that representing the yield point of the metal in the fully annealed condition. The explanation of this result is undoubtedly found in the study of Fig. 6 which reveals that the grain of the steel had increased to almost the equivalent of the thickness of the plate." I should like to point out that the results must also be influenced by the type of constituent (hence its properties) developed at 1100 degrees Cent. (2010 degrees Fahr.). Lower nitrogen-chromium steel shows the presence of some constituent at the grain boundaries. The grains, themselves, seem to be composed of chromium-nitrogen ferrite. In case of high nitrogen steel, similarly treated, we find in addition to ferrite a large amount of austenite. I wish to mention that Mr. Franks recognizes further down in his paper the difference in the constituents of high and low nitrogen alloys and suggests that austenite produces a keying action and greatly reduces the tendency to form grains on heating. This alone would hardly explain such vast difference in properties.

The conclusion derived from Mr. Franks' work and from this eager and free discussion on my part must be that the addition of nitrogen to chromium steels is definitely a promising feature insofar as the mechanical properties are concerned. The value of chromium alloys is in their stainlessness. It is therefore logical that Mr. Franks has looked into that matter. Speaking of corrosion resistance, he writes that the indications are that nitrogen does not

seriously affect this property of the steel. This very question has been carefully ascertained and for the benefit of those who are interested in this subject, I submit the results of work on five alloys of variable composition. The corrosive medium was 65 per cent boiling nitric acid.

Sample	Carbon	Chromium	Nitrogen	Inches Penetration per month
A	0.021	18.84	Nil	0.0031
B	0.202	18.77	Nil	0.036
C	0.012	18.26	0.009	0.0032
D	0.008	18.26	0.145	0.0045
E	0.014	18.06	0.213	0.0078

The above results represent an average of 4 specimens, each of the four, however, being in good agreement with the other three. One may conclude that the influence of nitrogen toward resistance to nitric acid is definitely less harmful than that of carbon. If nitric acid tests are to serve as a criterion of resistance to corrosion to other media then the additions of nitrogen are not harmful. The interest of myself and my associates in the work of Mr. Franks is so profound that we sincerely hope to hear from him again either next year or, preferably, sooner.

Oral Discussion

A. C. JONES:[2] I have not had the opportunity of reading this paper and therefore my discussion will be limited and perhaps subject to correction by the author. I wish to speak only on the effects of nitrogen on the soundness of chromium alloy castings.

We made some experimental heats in our high frequency furnace with varying chromium contents, particularly the 13 per cent chromium, 0.12 carbon maximum type and the 25 per cent chromium, 1.00 per cent nickel, 0.25 per cent carbon alloy. A virgin charge was used and the chromium and nitrogen contents obtained by the use of a 70 per cent ferrochromium carrying 0.06 per cent carbon and 0.77 per cent nitrogen. In the case of the 13 per cent chromium composition, this yielded a calculated nitrogen content of 0.15 per cent; and for the 25 per cent chromium alloy roughly 0.28 per cent.

It was found that castings of the 13 per cent chromium metal were quite porous while those of the higher chromium analysis were in most cases free, but showing a slight tendency to have gas-holes. Apparently it is necessary to maintain nitrogen contents appreciably lower than those I have just mentioned in order to be free of any tendency to unsoundness.

The benefit of nitrogen in grain refinement of 26 per cent chromium castings is appreciable and, particularly when pouring at the higher temperatures.

W. B. ARNESS:[3] This paper was to me one of the most interesting that has recently appeared. The recognition of the influence of nitrogen upon the physical properties of the iron-chromium stainless steels of low carbon content marks an important advance in our knowledge and use of these steels. One thing that particularly impresses me is the economic soundness of this development, wherein little or no added expense is imposed through its adoption.

I should like to ask if Mr. Franks has observed what is approximately

[2]Metallurgist, Lebanon Steel Foundry, Lebanon, Pa.

[3]Metallurgist, Rustless Iron Corporation of America, Baltimore, Md.

the maximum amount of nitrogen that can be dissolved by the iron-chromium stainless steels, and particularly how this saturation point varies with chromium content. Presumably it should increase with increasing chromium, and when exceeded the soundness of the metal would probably be adversely affected. In other words, what is the maximum amount of nitrogen that can be added to stainless steels varying in chromium content from about 12 per cent to about 28 per cent without affecting physical soundness and density of the steel?

Author's Closure

Mr. Newell's comments concerning the influence of nitrogen on high chromium steels or irons are greatly appreciated. He has pointed out undoubtedly one of the most important beneficial effects of nitrogen by reference to the difficulty met with in cold drawing the steels containing in the vicinity of 25 per cent chromium because of the large grains that frequently occur in hot-rolled articles of the steels. The experience with these steels has shown that even though they are reduced in cross section to a considerable degree by hot working, recrystallization resulting in the formation of large grains often occurs on annealing. This does not take place throughout the entire section of a hot-rolled and annealed article, although that portion of the article which recrystallizes hinders further work due to the brittleness of the metal. A good many hot-rolled articles of high nitrogen steels having a similar chromium content have been made, and in no instance has this development of large grains been found to occur.

Mr. Newell is quite right in bringing out that when these alloy steels contain 0.30 to 0.34 per cent nitrogen they are not as soft and ductile as those containing in the neighborhood of 0.20 per cent of this element. He finally mentions an application in which nitrogen will provide improved service. This is in weld overlays that are required to withstand the combined action of heat and abrasion. We have found that deposits having excellent resistance to abrasion may be obtained on surfaces by coating them with high nitrogen chromium-bearing steel welding rods.

Mr. Wright mentions the improvement to be secured by adding nitrogen to the 25 per cent chromium steels that are employed in the form of seamless tubes, and as in Mr. Newell's instance we are pleased to receive the opinion of those experienced in the manufacture of high chromium steel articles. It is apparent that Mr. Wright has also noticed that nitrogen additions have rendered the 25 per cent chromium steel far more adaptable to deep drawing operations. His comments concerning the welding characteristics of the high nitrogen-chromium steels give indication of a wider field of usefulness for the steels. He further agrees that nitrogen does not decrease the oxidation resistance of the steels at elevated temperatures, a fact fully confirmed in various tests at the temperatures at which steels of this type are used.

Dr. Krivobok's able discussion of this paper should be thoroughly considered by all those interested in nitrogen additions to the high chromium steels. The first point he brings up is in connection with the apparent tendency of the nitrides to promote austenitic formation. The primary reason for bringing out this point in the paper was the fact that the nitrides do go into solid solution in high chromium iron at elevated temperatures, and act

in a way similar to that of carbides in ordinary iron. His criticism pertaining to definite relationships between nitrogen and chromium is undoubtedly justifiable from a theoretical viewpoint. However, this method of specifying the nitrogen content to be employed in a given steel was used so as to provide a simple basis for practical application. It is quite true that the amount of nitrogen to be included in a steel should depend on the properties desired, and such information will eventually be obtained by those interested in the steels.

Dr. Krivobok strongly infers that the high nitrogen-chromium alloy steels are more brittle than similar steels of low nitrogen content. We have not found this to be true even under most conditions, provided the steels have the proper nitrogen contents. An important point in this connection is the percentage of carbon that is also present in the high nitrogen alloy steels. One of the objects of this paper was to point out the effects of nitrogen in low carbon high chromium steels, and the data show that if the carbon content is kept low, strong, ductile, and tough high chromium alloy steels can be obtained by using judicious amounts of nitrogen. If, for example, an 18 per cent chromium steel containing 0.15 per cent carbon is treated with nitrogen the resulting steel will possess little toughness due primarily to the carbon content rather than to the nitrogen content of the steel. On the other hand, if nitrogen is incorporated in a similar steel containing 0.07 per cent carbon, the metal will exhibit considerable toughness with relatively high strength and ductility. The data given by Dr. Krivobok in regard to the influence of nitrogen on the corrosion-resisting properties of the high chromium steels are certainly appreciated. As shown in his table, he selected extremely low carbon steels containing different percentages of nitrogen, and none of the steels were badly attacked by boiling 65 per cent nitric acid, while a similar chromium steel containing 0.20 per cent carbon and very little nitrogen was badly corroded. As Dr. Krivobok states, the question of whether the results of the nitric acid test serve as a criterion of resistance to corrosion in other media is problematical. It is generally recognized that the plain high chromium steels are designed primarily to resist the oxidizing type of corrosion, and in view of this evidence nitrogen does not seriously impair the utility of the steels.

Mr. Jones mentions in his discussion two chromium steels that probably contain too much nitrogen for commercial application. Mr. Arness seeks information in regard to the maximum amount of nitrogen that can be added to stainless steels varying in chromium content between 12 and 28 per cent without affecting physical soundness and density of the steel. We refer him to the closing paragraphs of the paper for answers to this question.

In closing the discussion of this paper we should like to point out that the object of adding nitrogen in the form of nitrides to these high chromium steels is because of the apparent high solubility of the nitrides in high chromium irons and steels, and the effect that this has upon grain structure. In order to secure the full benefit of the nitrides from the standpoint of toughness it is recommended that they be added to steels of comparatively low carbon contents, because in no case has it been found that nitrogen will correct the harmful influence that carbon exerts in many instances on steels that are relatively high in chromium.

INFLUENCE OF CARBON CONTENT ON HIGH TEMPERATURE PROPERTIES OF STEELS

By A. E. White, C. L. Clark and R. L. Wilson

Abstract

This paper presents results which show the influence of carbon content on the high temperature characteristics of two grades of steel, one of which was of the plain carbon type and the other a low alloy steel containing silicon, chromium and molybdenum. In each case two carbon contents were considered with the lower carbon steels containing approximately 0.10 per cent and the higher, 0.45 per cent.

The comparisons are based on the short-time tensile, creep and impact characteristics at temperatures ranging from 85 to 1400 degrees Fahr. (30-760 degrees Cent.). The relative high temperature stability of the steels was also investigated by submitting specimens after creep testing to metallographic examination and to tensile and impact tests at room temperature.

The results indicate that the behavior of steels at elevated temperatures is sometimes independent of the carbon content and may be affected by initial heat treatments or the addition of alloying elements that would change the character of the carbides in the structure.

Introduction

MANY conflicting statements have been made as to the influence of carbon content on the high temperature characteristics of steels, especially with respect to the creep resistance. There is meager information in the literature on the effect of carbon on the high temperature properties of alloy steels, but researches of this nature have been conducted on plain carbon steels. Tapsell[1] has stated that while increased carbon content in plain carbon steel is beneficial at

[1] "Creep of Metals," 1931, p. 215.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago from September 30 to October 4, 1935. Of the authors, Dr. A. E. White is Director, Department of Engineering Research, University of Michigan, C. L. Clark is Research Engineer, Department of Engineering Research, University of Michigan, Ann Arbor, Michigan, and R. L. Wilson is Metallurgical Engineer, The Timken Steel and Tube Company, Canton, Ohio. Manuscript received June 3, 1935.

lower temperatures, not much creep strength is gained at temperatures greater than 450 degrees Cent. (840 degrees Fahr.) by increasing carbon content above 0.40 per cent. Data provided by Norton[2] indicate that at 1000 degrees Fahr. (540 degrees Cent.) the creep strength is increased as the carbon content is raised from 0.08 to 0.42 per cent.

Grün[3] investigated low carbon steels at 400 and 500 degrees Cent. (750 to 930 degrees Fahr.) and found that while the tensile strength and elastic limit increased considerably with increasing carbon content, the creep strength increased much less and even decreased with more than 0.30 per cent carbon. Juretzek and Sauerwald[4] conducted creep tests on several steels at 400, 500 and 550 degrees Cent. (750, 930 and 1020 degrees Fahr.) and found the creep strength to increase with increasing carbon content.

While many such researches could be quoted, those given are sufficient to show that claims have been made that carbon increases, decreases, or has no appreciable influence on creep resistance.

The subject is further complicated by the fact that complete information is not always available on the steels being compared and the conclusions may therefore be influenced by variables other than the carbon content. For example, it has been previously pointed out by the authors that two plain carbon steels with identical carbon content may possess entirely different creep characteristics, depending upon whether they are "open" or "killed". In many comparisons the higher carbon steels are fully killed while the lower carbon steels are open or rimmed. Appreciable amounts of other elements, such as manganese and silicon, may also affect the findings. Other variables such as the melting process employed, casting practice, mechanical working, grain-size, and heat treatment must be substantially the same if the true influence of carbon content alone is to be obtained.

The purpose of the present paper is to offer additional information on this subject gathered from tests on both plain carbon and a low alloy steel that are essentially the same in all respects except for difference in carbon content. Comparisons of high temperature properties are based on short-time tensile, impact, and creep tests.

---

[2] "Creep of Steel at High Temperatures," 1929, p. 88.

[3] "The Creep Strength of Steels as Dependent on Alloy and Heat Treatment," Arch. Eisenhüttenw. 8: 205-11, 1934.

[4] "Creep Resistance of Structural Steel and a Simplified Testing Method," Die Wärme, 57: 267-73, 1934.

To determine the influence of carbon content upon the structural stability as well, the specimens used for the creep tests were subjected to tensile and impact tests at room temperature and to metallographic examination.

Steels Investigated

Two types of steel were investigated, one was plain carbon and the other a low alloy silicon-chromium-molybdenum steel. Two carbon contents were selected in each type, the lower being approximately 0.10 per cent and the higher 0.45 per cent. The designation, chemical composition, method of manufacture, heat treatment, Brinell hardness and grain-size of these steels are given in Table I.

In order to eliminate major variations in material incidental to manufacturing methods all the steels were obtained from the same source, namely The Timken Steel and Tube Company. The steels

Table I
Chemical Composition, Method of Manufacture, Heat Treatment, Brinell Hardness and Grain-Size

Designation	Chemical Composition							Method of Manufacture	Brinell Hardness	Grain-Size
	C	Mn	Si	S	P	Cr	Mo			
1015*	0.15	0.46	0.28	0.021	0.019	....	...	O.H.	111	5-6
1040*	0.43	0.67	0.20	0.033	0.035	....	...	O.H.	167	4-5
Si-Cr-Mo (0.07C)*	0.07	0.42	0.72	0.015	0.014	1.25	.54	E.F.	123	4-5
Si-Cr-Mo (0.48C)†	0.48	0.49	0.62	0.015	0.016	1.20	.52	E.F.	197	4-5

*Annealed at 1550 degrees Fahr. (845 degrees Cent.).

†This steel was annealed at 1550 degrees Fahr. (845 degrees Cent.) and then tempered at 1380 degrees Fahr. (750 degrees Cent.) to obtain complete softening.

O.H. = Open-hearth steel.

E.F. = Electric furnace steel.

were hot-rolled into 1-inch round bars and were heat treated in this size. The necessary specimens were machined after the heat treatment.

Insofar as the chemical composition is concerned, the chief difference in the steels of each type is in the carbon content. The 1040 material possesses a somewhat higher manganese content than the 1015 analysis, but it is believed that this difference is not great enough to change the results appreciably. The steels were given an identical heat treatment, which consisted of annealing from 1550 degrees Fahr. (845 degrees Cent.). Normal slow cooling from this annealing temperature left all the steels fully softened except the 0.45 per cent carbon Si-Cr-Mo steel that had to be tempered at 1380 degrees Fahr.

(750 degrees Cent.) after annealing to become as completely stabilized as the other steels.

The metallographic structures produced by the annealing treatments are shown at a magnification of 1000 diameters in the four photomicrographs of Figs. 1 to 4. In the two carbon steels the pearlite is definitely laminated while in the two alloy steels it is spheroidized. The double annealing treatment to which the higher carbon alloy steel was subjected would tend to produce a spheroidized structure, but it is evident from Figs. 3 and 4 that a similar structure has also resulted from the simple annealing treatment given to the lower carbon alloy steel.

From the preliminary examinations the steels appear to be well suited for the purpose of determining the influence of carbon content on behavior at high temperatures as all of the known variables, with the exception of this factor, have been largely eliminated.

Experimental Results

As the construction of much high temperature equipment is still designed upon the short-time tensile, rather than the creep characteristics, it was deemed advisable to consider both of these properties. Likewise, since the ability to resist shock is oftentimes an important factor, the influence of carbon content on the impact resistance was investigated. Tensile and impact tests at room temperature and metallographic examination of the creep specimens after creep testing were included to find whether carbon content exerted an influence upon the structural stability of the steels under the combined action of stress and temperature.

Short-Time Tensile Properties

Short-time tensile tests were conducted on each of the four steels at temperatures ranging from 80 to 1400 degrees Fahr. (26 to 760 degrees Cent.). Standard 0.505-inch diameter specimens were used and the procedure was in accordance with the Tentative Specification of the A.S.T.M.-A.S.M.E. High Temperature Committee (E21-34T). Duplicate tests were made at each temperature and the proportional limit and yield stress values were determined in addition to the usual tensile properties. An optical extensometer system was used for determining the stress-strain curves which is sensitive to 2.8 millionths of an inch per inch of two inch gage section. The

Figs. 1 and 2—Metallographic Structures of Plain Carbon and Si-Cr-Mo Steels with Varying Carbon Content—× 1000. Fig. 1—Steel 1015. Fig. 2—Steel 1040.

Figs. 3 and 4—Metallographic Structures of Plain Carbon and Si-Cr-Mo Steels with Varying Carbon Content—× 1000. Fig. 3—Si-Cr-Mo Steel (0.07% Carbon). Fig. 4—Si-Cr-Mo Steel (0.48% Carbon).

Table II

Influence of Carbon Content and Temperature on the Tensile Properties of Carbon Steel (Annealed)

Steel	Temperature Degrees Fahr.	Tensile Strength Lb./Sq.In.	Yield Stress Lb./Sq.In. 0.2%	Yield Stress Lb./Sq.In. 0.1%	Proportional Limit Lb./Sq.In.	Per Cent Elongation in 2 Inches	Per Cent Reduction of Area
1015	80	57,325	34,125	32,375	15,875	39.5	67.65
1040	80	88,850	44,625	44,000	32,500	26.0	42.1
1015	750	51,525	17,625	16,375	10,000	41.25	71.4
1040	750	77,362	30,800	28,000	15,625	31.5	60.2
1015	900	38,725	16,700	15,375	8,125	46.5	79.6
1040	900	58,325	26,550	24,300	11,250	33.0	59.85
1015	1000	30,525	13,500	12,375	5,000	53.0	83.45
1040	1000	48,375	21,625	19,125	6,000	34.75	54.45
1015	1100	23,050	10,125	9,350	3,000	65.0	88.95
1040	1100	35,275	16,025	13,950	4,500	39.25	56.25
1015	1200	16,275	7,100	6,250	1,000	70.75	92.5
1040	1200	25,400	11,375	9,950	4,000	48.0	64.85
1015	1300	11,350	4,750	4,375	0.00	81.25	95.5
1040	1300	17,100	8,750	7,375	0.00	39.25	50.75
1015	1400	8,525	3,550	3,150	0.00	79.25	78.5
1040	1400	13,575	6,000	5,100	0.00	83.0	93.0

results obtained are presented in Figs. 5 to 8, inclusive, and Tables II and III.

Considering the carbon steels first, it is evident that the higher carbon material possesses the higher tensile strength and yield stress values over the entire temperature range, with its superiority being the more marked at the lower temperatures. The same is likewise true with the proportional limit values at temperatures of 900 degrees Fahr. (480 degrees Cent.) or lower. At the higher temperatures carbon exerts little influence on the proportional limit values, although in the majority of cases the higher carbon steel possesses slightly

Table III

Influence of Carbon Content and Temperature on the Tensile Properties of Si-Cr-Mo Steels (Annealed)

Steel	Temperature Degrees Fahr.	Tensile Strength Lb./Sq.In.	Yield Stress Lb./Sq.In. 0.2%	Yield Stress Lb./Sq.In. 0.1%	Proportional Limit Lb./Sq.In.	Per Cent Elongation in 2 Inches	Reduction of Area Per Cent
Si-Cr-Mo (0.07C)	80	66,500	35,200	34,300	24,000	36.5	72.7
Si-Cr-Mo (0.48C)	80	97,050	45,000	44,425	32,500	25.5	48.95
Si-Cr-Mo (0.07C)	750	71,650	26,400	25,450	18,000	27.0	67.8
Si-Cr-Mo (0.48C)	750	85,850	31,875	28,750	17,500	31.0	62.3
Si-Cr-Mo (0.07C)	900	67,525	25,600	24,150	18,000	25.75	66.35
Si-Cr-Mo (0.48C)	900	69,625	28,700	26,025	15,625	35.25	72.45
Si-Cr-Mo (0.07C)	1000	57,750	24,900	23,500	15,000	25.5	73.3
Si-Cr-Mo (0.48C)	1000	57,975	24,350	22,350	12,500	42.5	81.15
Si-Cr-Mo (0.07C)	1100	47,500	23,100	22,500	13,500	31.0	82.55
Si-Cr-Mo (0.48C)	1100	43,725	19,025	17,475	8,500	50.75	88.4
Si-Cr-Mo (0.07C)	1200	33,275	16,000	14,000	3,500	36.5	88.2
Si-Cr-Mo (0.48C)	1200	31,925	14,350	13,250	5,500	59.25	91.55
Si-Cr-Mo (0.07C)	1300	22,775	11,100	10,200	2,250	61.75	94.5
Si-Cr-Mo (0.48C)	1300	23,850	10,625	9,125	0.00	66.0	93.3
Si-Cr-Mo (0.07C)	1400	13,800	7,000	5,950	1,500	72.25	98.35
Si-Cr-Mo (0.48C)	1400	16,050	7,250	5,625	0.00	76.5	92.75

higher values. As might be expected, increase in carbon content has reduced the ductility of the steel over most of the temperature range explored. The lower carbon steel possesses the greater elongation and reduction of area values at all temperatures except 1400 degrees Fahr. (760 degrees Cent.). This happens because at 1400 degrees Fahr. the 1040 steel has already transformed while the 1015 steel is still within its thermal critical range.

The high temperature tensile properties of the Si-Cr-Mo steels are given in Figs. 7 and 8. At the lower temperature, the steel containing 0.45 per cent carbon has the greater strength. However, at

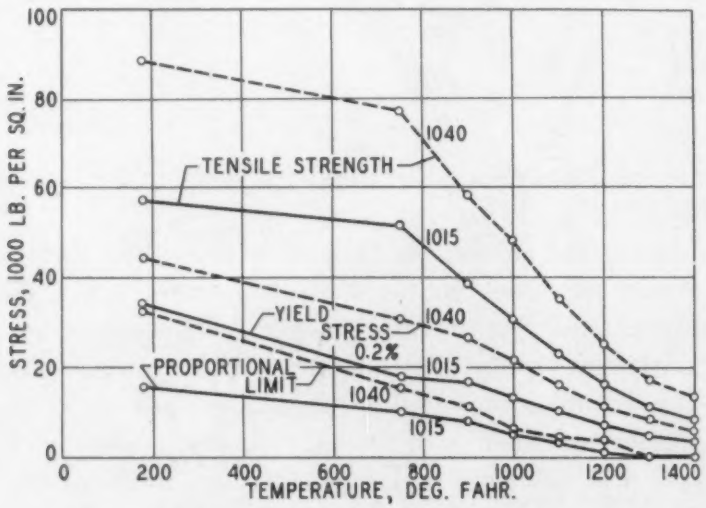


Fig. 5—Influence of Carbon Content and Temperature on the Strength Characteristics of Carbon Steel (Annealed).

temperatures of 900 degrees Fahr. (480 degrees Cent.) and higher, the strength of these alloys seems to be independent of carbon content. The same is true in the case of the proportional limit even at 750 degrees Fahr. (400 degrees Cent.). On the contrary, at room temperature the lower carbon steel exhibits greater elongation and reduction of area, while at practically all of the remaining temperatures the higher carbon steel has the superior values.

In reviewing the results of the short-time tensile tests, it would seem to be necessary to differentiate between the behavior of all the steels from room temperature to about 900 degrees Fahr. and from 900 degrees Fahr. (480 degrees Cent.) up to the carbon change-point. In the temperature range from room temperature to 900 degrees Fahr., increase in carbon content of the steels, regardless of the structure, confers greater strength with corresponding decrease in

ductility. At temperatures from about 900 degrees Fahr. (480 degrees Cent.) to the transformation range, higher strength follows increase in carbon only when the structure of the steel contains lamellar pearlite. Nevertheless, in any combination of circumstances lower

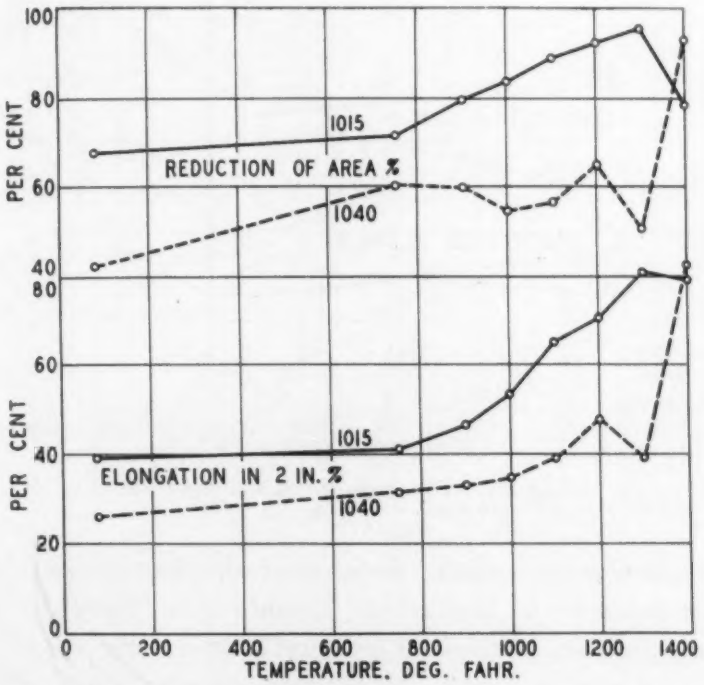


Fig. 6—Influence of Carbon Content and Temperature on the Ductility of Plain Carbon Steel (Annealed).

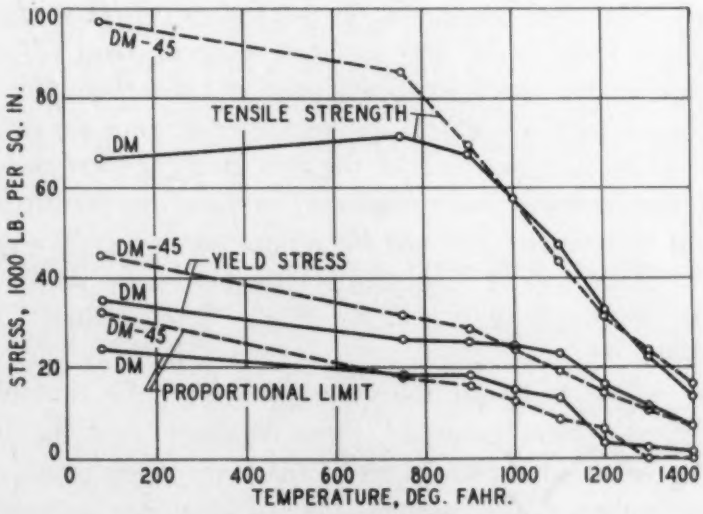


Fig. 7—Influence of Carbon Content and Temperature on the Strength Characteristics of Si-Cr-Mo Steel.

ductility accompanies increase in strength. Finally, it appears that the form in which the carbides occur in the structure will affect the high temperature mechanical properties of pearlitic steels at least.

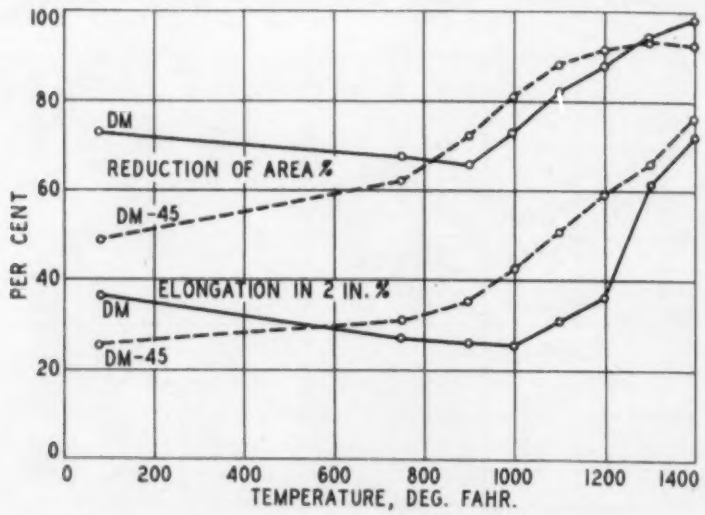


Fig. 8—Influence of Carbon Content and Temperature on the Ductility of Si-Cr-Mo Steel.

Initial heat treatments and the addition of alloying elements that may change the character of the carbide formation can therefore influence the tensile properties of steels at elevated temperatures.

Creep Characteristics

Creep tests were conducted on the four steels at 800, 1000 and 1200 degrees Fahr (425, 540 and 650 degrees Cent.). Standard 0.505-inch diameter specimens were used and the elongation or creep was measured with an optical extensometer system sensitive to 2.8 millionths of an inch per inch of the two inch gage length. At least four different stresses were employed at each temperature and the majority of tests were continued for a minimum of 1000 hours. The testing procedure was in accordance with the Tentative Specification of the Joint A.S.T.M.-A.S.M.E. High Temperature Committee (E22-34T).

Space will not permit the inclusion of all the time-elongation curves, but, as typical examples, those obtained from the 1040 steel at 1000 degrees Fahr. (540 degrees Cent.) are given in Fig. 9. The creep rates in the so-called second stage of creep are indicated on the curves. Although there are several different ways of interpreting

creep data, all the comparisons made here are based on the rates of creep observed in the second stage of creep.

The creep rates and the corresponding unit-stresses were then plotted to logarithmic coordinates, as shown in Figs. 10 and 11. This

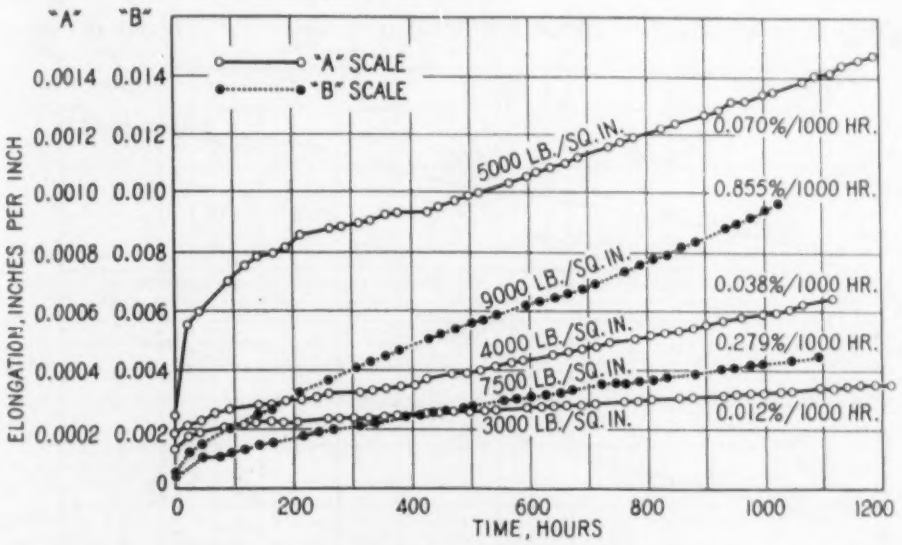


Fig. 9—Time-Elongation Curves at 1000 Degrees Fahr. for 1040 Steel. (Annealed).

procedure was employed since in many cases approximately straight-line curves result, from which the stresses corresponding to definite rates of creep can, within certain limits, be obtained.

A logarithmic plot of the results for the two carbon steels is shown in Fig. 10 and stress values obtained from these curves, for creep rates of 0.01, 0.10 and 1.0 per cent per 1000 hours, are given in Table IV. At all three temperatures, the higher carbon 1040 steel possesses the greater creep resistance, with its superiority being

Table IV

Influence of Carbon Content and Temperature on the Creep Characteristics of Carbon Steel (Annealed)

Steel	Temperature Degrees Fahr.	Stress for Designated Creep Rate Per Cent per 1000 Hours 0.01	0.10	1.0
1015	800	12,000	17,200	25,500
1040	800	13,000	18,500	27,000
1015	1000	1,800	3,300	6,000
1040	1000	2,800	5,550	9,300
1015	1200	140	540	2,100
1040	1200	140	860	2,650

the more marked at 1000 degrees Fahr. (540 degrees Cent.). At 1200 degrees Fahr. (650 degrees Cent.), these two steels have approximately the same value for the slowest creep rate considered.

Similar data for the two alloy steels are given in Fig. 11 and Table V. In this case the lower carbon material possesses the greater creep resistance at all three temperatures with the largest difference

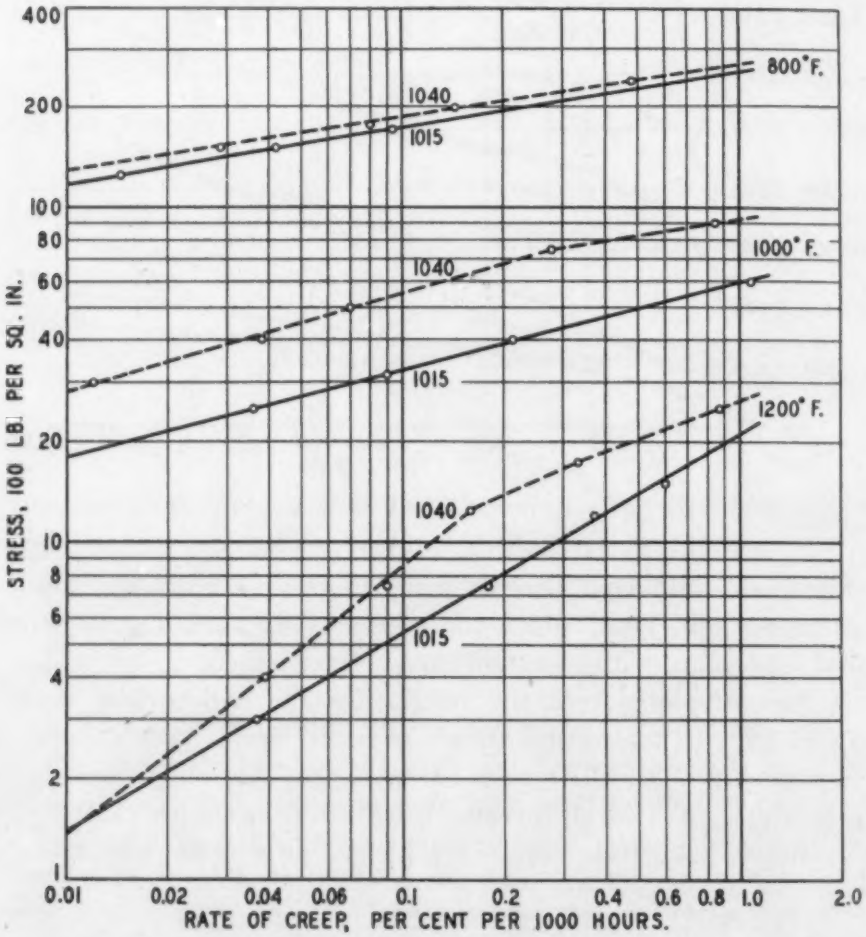


Fig. 10—Creep-Stress Curves Showing Influence of Carbon on the Creep Strength of Carbon Steels at Indicated Temperatures.

being at 1000 degrees Fahr. (540 degrees Cent.). In fact, the creep strength of the lower carbon steel at 1000 degrees Fahr. (540 degrees Cent.) is nearly equal to that of the higher carbon material at 800 degrees Fahr. (425 degrees Cent.).

The condition of the carbides again seems to be important. When the carbides are in lamellar form the structure offers the best resistance to creep. In the case of the plain carbon steels, both of

Table V

Influence of Carbon Content and Temperature on the Creep Characteristics of Si-Cr-Mo Steel (Annealed)

Steel	Temperature Degrees Fahr.	Stress for Designated Creep Rate Per Cent per 1000 Hours 0.01	0.10	1.0
Si-Cr-Mo (0.07C)	800	20,000	29,000	42,500
Si-Cr-Mo (0.48C)	800	15,000	24,500	40,000
Si-Cr-Mo (0.07C)	1000	13,000	22,500	38,000
Si-Cr-Mo (0.48C)	1000	4,100	8,200	15,000
Si-Cr-Mo (0.07C)	1200	1,950	3,950	8,100
Si-Cr-Mo (0.48C)	1200	1,000	2,200	4,800

which had a lamellar pearlitic structure originally, the 0.45 carbon steel having more lamellar pearlite showed better creep strength than the 0.15 per cent carbon steel until effective spheroidization at 1200 degrees Fahr. (650 degrees Cent.) equalized the long-time loading capacity of the steels. The extent of the spheroidization in the 1040

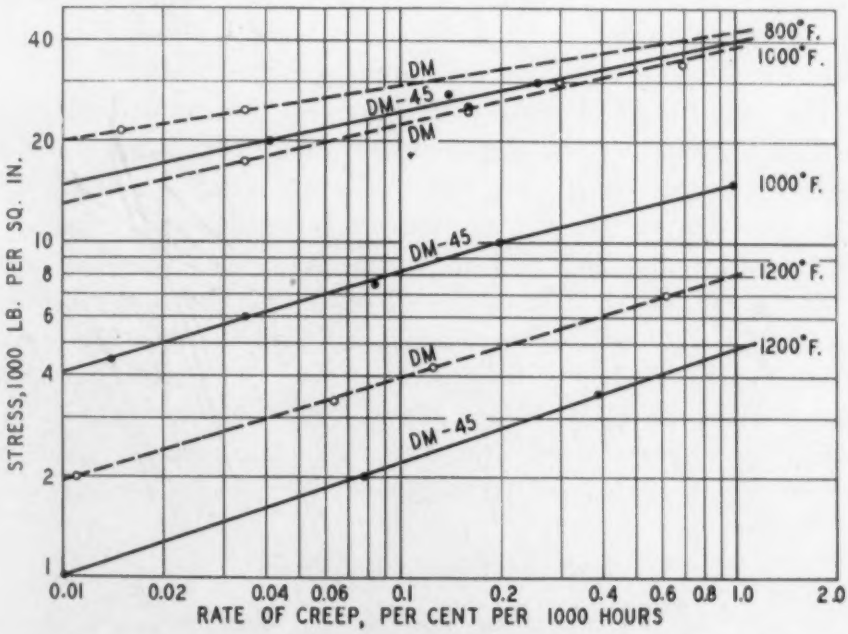


Fig. 11—Creep-Stress Curves Showing Influence of Carbon on the Creep Strength of Si-Cr-Mo Steels at Indicated Temperatures.

steel can be seen in the photomicrograph of Fig. 14, which should be compared with the photomicrograph of Fig 2. The two Si-Cr-Mo steels were in the early stages of spheroidization as a result of the preliminary annealing treatment, and it may be supposed that the differences in creep strength involve the relative rates of carbide

agglomeration. Apparently, increase in carbon content only raises the creep strength of pearlitic steels when the structure of the steels is not in the most stable condition.

Impact Resistance

The Charpy impact resistance of the steels was determined over the temperature range of 75 to 1200 degrees Fahr (25-650 degrees Cent.). The keyhole notch was used and the specimens were heated in a nearby furnace for one hour, transferred to the machine and broken. The time involved in removing the specimens from the furnace and breaking them was approximately 4 seconds. All the tests were conducted in triplicate and the results obtained are given in Figs. 15 and 16.

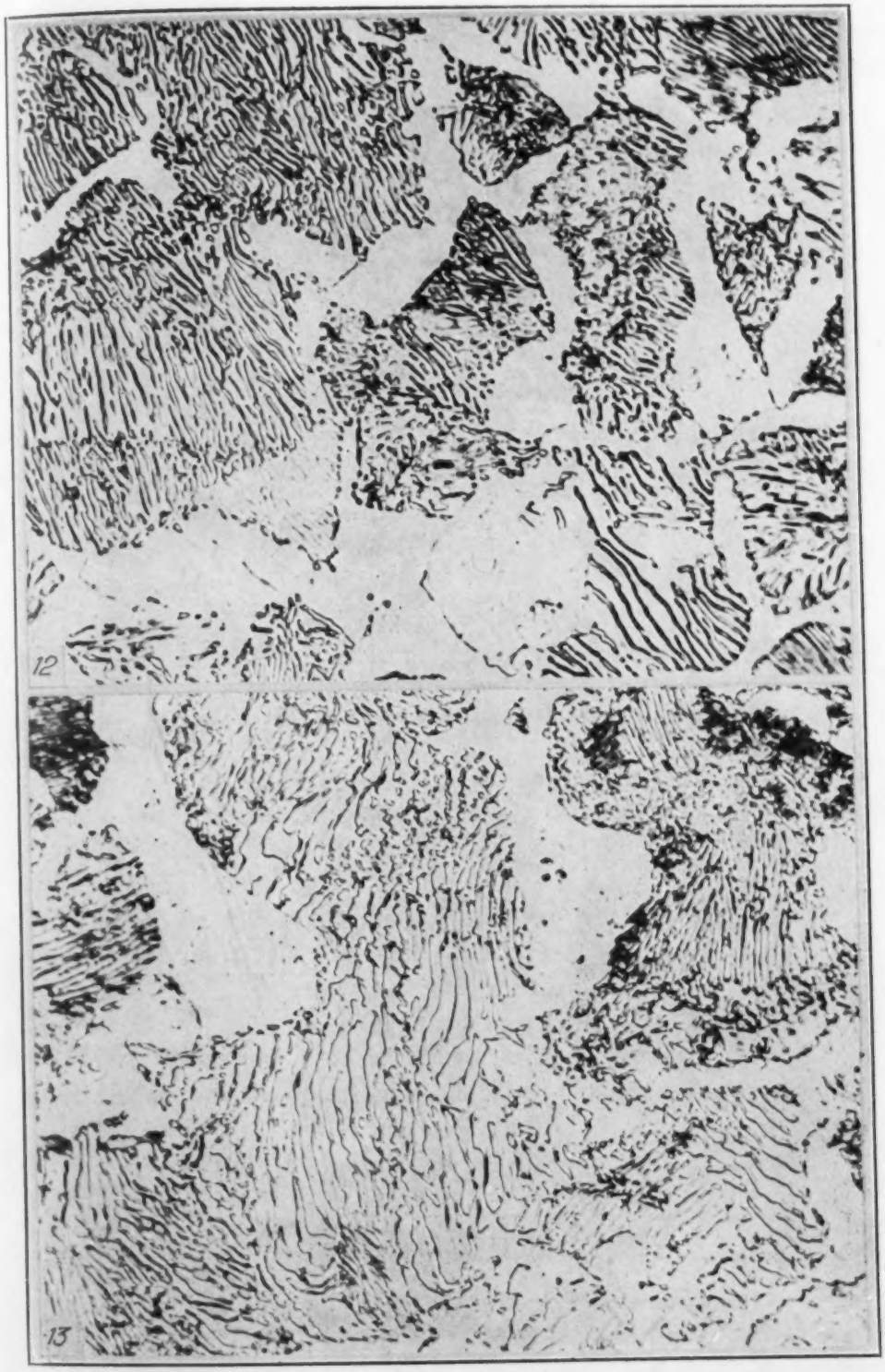
The results from the plain carbon and Si-Cr-Mo steels are in agreement in that in both cases the lower carbon materials possess the higher resistance to impact. Over the major portion of the temperature range, however, the differences due to carbon content are greater for the alloy type than for the plain carbon type.

The four curves of these two figures are similar and all show a minimum at 900 to 1100 degrees Fahr. (480-595 degrees Cent.). This condition also exists for practically all pearlitic steels studied previously. Carbon content may have somewhat of an influence on the temperature at which this minimum occurs as increasing carbon content appears to shift it in the direction of higher temperature. For example, with the lower carbon alloy steel the minimum occurs at 1000 degrees Fahr. (540 degrees Cent.) and with the higher carbon analysis at 1100 degrees Fahr. (595 degrees Cent.). The corresponding temperatures for the two plain carbon steels are 900-1000 degrees Fahr. and 1000 degrees Fahr. (540 degrees Cent.).

High Temperature Stability

In order to determine the influence of time, temperature and stress on the stability of steels, the creep specimens were subjected after creep testing to a metallographic examination and to short-time tensile and impact tests at room temperature.

(a) Metallographic Examination: Longitudinal sections were taken at the center of the gage length of two creep specimens from each temperature and examined at magnifications of 100 and 1000 diameters. Space will not permit the inclusion of all the resulting



Figs. 12 and 13—Influence of Creep Tests on the Metallographic Structure of 1040 Steel—× 1000. Fig. 12—Creep Specimen at 800 Degrees Fahr. 24,000 Pounds Per Square Inch—1025 Hours Duration. Fig. 13—Creep Specimen at 1000 Degrees Fahr. 5000 Pounds Per Square Inch—1190 Hours Duration.

Fig. 14—Influence of Creep Tests on the Metallographic Structure of 1040 Steel —× 1000. Creep Specimen at 1200 Degrees Fahr. 1750 Pounds Per Square Inch—1100 Hours Duration.

photomicrographs, but as a typical example, certain of those obtained from the 1040 steel are shown in Figs. 12, 13 and 14.

If these are compared with photomicrograph of Fig. 2 it will be evident that the creep tests at 800 and 1000 degrees Fahr. (425-540 degrees Cent.) have produced no apparent structural changes. The creep tests at 1200 degrees Fahr. (650 degrees Cent.) did, however, in that the pearlite was changed from the lamellar to the spheroidized condition. The structure is in the early stages of spheroidization as no appreciable migration of the spheroidized particles to the grain boundaries has occurred.

The results obtained from the remaining three steels were similar. Since the initial structures of the two Si-Cr-Mo steels were partially spheroidized the observed changes were not as marked. The creep tests at 1200 degrees Fahr. (650 degrees Cent.) did, however, cause a decided increase in the degree of spheroidization although no appreciable migration of the carbides to the grain boundaries was observed. The change consisted mainly of the carbide particles assum-

Table VI

Influence of Carbon Content on the Tensile Properties of Plain Carbon and Si-Cr-Mo Steels Before and After Creep Tests at 800, 1000 and 1200 Degrees Fahr.

Steel	Creep Tests Temperature Degrees Fahr.	Creep Tests Stress Lb./Sq.In.	Tensile Strength Lb./Sq.In.	Yield Stress Lb./Sq.In.	Proportional Limit Lb./Sq.In.	Per Cent Elongation in 2 In.	Per Cent Reduction of Area
			Plain Carbon Steels				
1015	85	.....	57,325	34,125	15,875	39.5	67.7
1015	800	10,000	57,250	35,000	17,500	40.5	67.8
1015	800	12,500	57,250	35,000	17,500	40.0	67.4
1015	1000	2,500	56,500	35,000	20,000	41.0	69.6
1015	1000	3,200	55,750	32,500	17,500	38.5	67.8
1015	1200	750	51,850	35,000	17,500	36.5	74.6
1015	1200	1,500	48,400	32,500	15,000	39.5	78.0
1040	85	.....	88,850	44,625	32,500	26.0	42.1
1040	800	20,000	90,150	46,000	25,000	25.5	40.7
1040	800	15,000	90,300	44,000	25,000	25.5	39.2
1040	1000	7,500	86,450	44,000	32,500	25.5	43.5
1040	1200	750	68,050	34,000	20,000	26.0	60.8
1040	1200	1,250	69,600	38,000	25,000	27.5	62.4
			Si-Cr-Mo Steels				
Si-Cr-Mo (0.07C)	85	.....	66,500	35,200	24,000	36.5	72.7
Si-Cr-Mo (0.07C)	800	19,927	66,200	41,000	34,000	38.5	71.9
Si-Cr-Mo (0.07C)	800	24,800	65,400	38,000	34,000	37.0	72.3
Si-Cr-Mo (0.07C)	1000	17,500	68,100	39,000	30,000	36.0	71.2
Si-Cr-Mo (0.07C)	1100	24,600	66,875	40,000	36,000	35.5	72.7
Si-Cr-Mo (0.07C)	1100	8,000	68,450	41,250	30,000	34.5	72.3
Si-Cr-Mo (0.07C)	1200	4,000	62,950	38,000	30,000	33.0	72.3
Si-Cr-Mo (0.07C)	1200	6,000	63,320	40,000	30,000	31.0	74.9
Si-Cr-Mo (0.48C)	85	.....	97,050	45,000	32,500	25.5	49.0
Si-Cr-Mo (0.48C)	800	27,500	92,350	45,000	25,000	27.5	54.9
Si-Cr-Mo (0.48C)	800	30,000	96,000	50,000	35,000	25.0	50.5
Si-Cr-Mo (0.48C)	1000	4,500	96,100	47,500	35,000	25.5	49.8
Si-Cr-Mo (0.48C)	1000	10,000	94,700	47,500	35,000	25.0	51.7
Si-Cr-Mo (0.48C)	1200	3,500	83,850	43,250	20,000	26.0	53.7
Si-Cr-Mo (0.48C)	1200	1,000	86,150	44,500	17,500	23.5	54.1

ing a more globular shape than in the case of the other steels.

On the basis of these findings, it may be concluded, therefore, that for these particular steels at least, the creep tests at 800 and 1000 degrees Fahr. (425-540 degrees Cent.) had no apparent influence on the resulting structure, while those at 1200 degrees Fahr. (650 degrees Cent.) did, in that either the pearlite was changed from a laminated to a spheroidized structure, or a greater degree of spheroidization was obtained, depending upon the original condition of the structure. Carbon content appears to be without effect in either hastening or retarding these changes under the given test conditions.

(b) Tensile Properties: Two creep specimens from each temperature were subjected to tensile tests at room temperature and the resulting values compared with those of the original material. The findings are given in Table VI.

In general the creep tests at 800 and 1000 degrees Fahr. (425-540 degrees Cent.) did not appreciably influence either the strength

or ductility characteristics. In certain cases the yield stress and proportional limit values were somewhat increased which may be accounted for by strain-hardening of the steel during the creep tests.

The creep tests at 1200 degrees Fahr. (650 degrees Cent.) caused a decrease in the tensile strength of the specimens when later

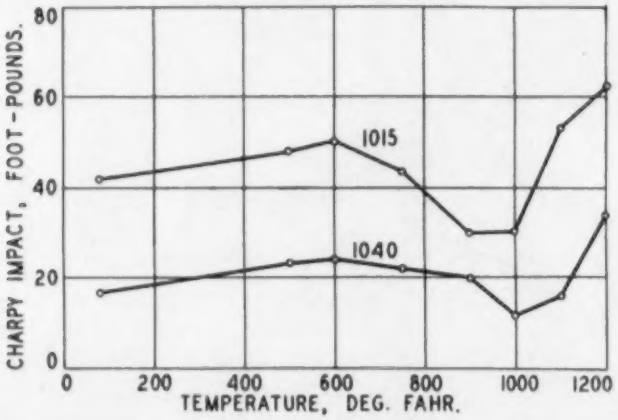


Fig. 15—Influence of Carbon Content on the High Temperature Impact Properties of Carbon Steel.

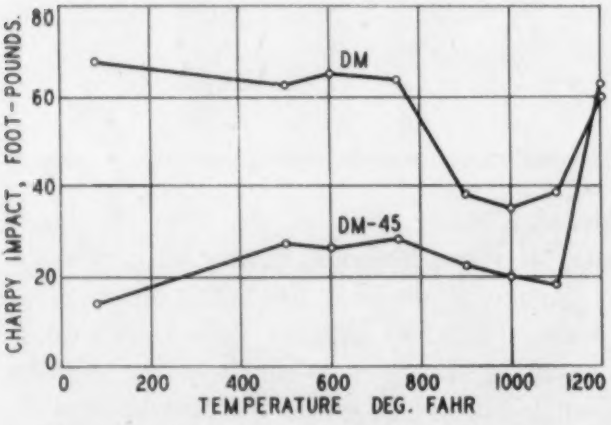


Fig. 16—Influence of Carbon Content on the High Temperature Impact Properties of Si-Cr-Mo Steels.

tested at room temperature with the low carbon Si-Cr-Mo steel undergoing the smallest loss and the 1040 steel the greatest. In most cases the yield stress and proportional limit values were not greatly affected although the proportional limits of the higher carbon Si-Cr-Mo steel and the 1040 steel were considerably reduced. This might indicate that increased carbon content decreases the stability of pearlitic steels under prolonged heating at 1200 degrees Fahr. (650 degrees Cent.). Elongation values were changed little, but in every

Table VII

Influence of Carbon Content on the Impact Resistance of Plain Carbon and Si-Cr-Mo Steels Before and After Creep Tests at 800, 1000 and 1200 Degrees Fahr.

Steel	Temperature Degrees Fahr.	Stress Lb./Sq.In.	Duration Hours	Izod Impact* Foot-Pounds
		Plain Carbon Steels		
1015	85	.....	....	73.5
1015	800	15,000	1065	73.5
1015	800	17,000	1020	77.0
1015	1000	4,000	1020	74.5
1015	1000	6,000	1005	74.0
1015	1200	300	990	77.0
1015	1200	1,200	985	80.0
1040	85	.....	....	19.0
1040	800	17,500	1025	20.5
1040	800	24,000	1025	18.5
1040	1000	5,000	1190	22.0
1040	1000	9,000	1020	24.0
1040	1200	400	1085	27.5
1040	1200	1,750	1100	26.5
		Si-Cr-Mo Steels		
Si-Cr-Mo (0.07C)	85	.....	...	90.5
Si-Cr-Mo (0.07C)	800	18,200	670	89.0
Si-Cr-Mo (0.07C)	800	21,800	625	89.3
Si-Cr-Mo (0.07C)	1000	10,260	525	87.3
Si-Cr-Mo (0.07C)	1000	20,500	525	90.5
Si-Cr-Mo (0.07C)	1100	6,000	1065	89.7
Si-Cr-Mo (0.07C)	1100	10,000	1335	90.1
Si-Cr-Mo (0.07C)	1200	2,000	500	90.0
Si-Cr-Mo (0.07C)	1200	4,200	650	89.3
Si-Cr-Mo (0.48C)	85	.....	....	16.0
Si-Cr-Mo (0.48C)	800	25,000	1025	16.0
Si-Cr-Mo (0.48C)	1000	6,000	1030	21.0
Si-Cr-Mo (0.48C)	1000	15,000	1100	19.0
Si-Cr-Mo (0.48C)	1200	2,000	1090	27.0
Si-Cr-Mo (0.48C)	1200	4,000	1160	22.5

*Average of two tests.

Note: Specimens used were smaller than standard.

case the reduction of area was larger, being the more marked for the two carbon steels.

(c) Impact Tests: Izod impact tests were conducted on the same two creep specimens used for the metallographic examination. Two specimens were machined from the gage section of the creep specimens and were, therefore, slightly smaller than standard dimensions. The results obtained are given in Table VII. Again it is to be noted that stressing the steels at 800 and 1000 degrees Fahr. (540 degrees Cent.) had no apparent influence on the cold impact resistance. After creep testing at 1200 degrees Fahr. (650 degrees Cent.), however, the impact resistance of three of the steels was increased; the exception was the lower carbon Si-Cr-Mo analysis, and in this case there was no change.

Conclusions

While the data obtained are not sufficiently extensive to permit broad generalizations they do indicate that behavior of steels at high temperatures depends not only upon the carbon content but also upon the temperature being considered, the condition of the carbides in the structure of the steel and the presence of alloying elements.

At temperatures up to 900 degrees Fahr. (480 degrees Cent.) increase in carbon content, regardless of the structure of the steels, increases short-time strength and decreases ductility. From about 900 degrees Fahr. (480 degrees Cent.) to the transformation range, higher strength and lower ductility result from increase in carbon content if the structure contains lamellar pearlite. When the structure is spheroidized, the carbon content has little influence on the strength or ductility of the steel at higher temperatures.

The effect of carbon content on the creep characteristics of the steels also depends upon the arrangement of the carbides in the pearlite. When the carbides are in lamellar form the resistance to creep is increased with higher carbon content. If the original structure is spheroidized, however, the creep resistance is reduced by increasing the carbon content. Under conditions favorable to spheroidization, a lamellar pearlitic structure may become spheroidized with attendant loss in creep strength, and in such instances resistance to creep is not improved by higher carbon content. This has happened in the case of the 0.45 per cent plain carbon steel in creep tests at 1200 degrees Fahr. (650 degrees Cent), where for the rate of 0.01 per cent per 1000 hours, the creep strength is the same as for the 0.15 per cent carbon steel.

In both the plain carbon and the low alloy steels, the lower carbon analyses possessed the higher impact properties both at room and elevated temperatures. A minimum occurred in the temperature range of 900 to 1100 degrees Fahr. (480-595 degrees Cent.), and it appears as if carbon content tends to raise the temperature at which this minimum occurs.

Carbon content appears to have little influence on the structural stability at elevated temperatures as is evident from the results of metallographic examination as well as tensile and Izod impact tests at room temperature on the creep specimens after creep testing. In all cases, the creep tests at 800 and 1000 degrees Fahr. (540 degrees Cent.) were without influence while those at 1200 degrees Fahr. (650

degrees Cent.) produced spheroidization with an accompanying decrease in tensile strength and an increase in the impact and reduction of area values.

It is a common experience that the addition of special elements to steels has been instrumental in creating alloys of greater creep strength. The observations made during this investigation may warrant the speculation that resistance to creep is enhanced by the effect these alloying elements may have on the normal structures of steels or on the diffusibility of the carbides.

Acknowledgments

The authors desire to express their appreciation to The Timken Steel and Tube Company for their financial assistance which has made these investigations possible and for their permission to publish the findings. Particularly do they wish to express their gratitude to F. J. Griffiths and H. H. Timken, Jr.

DISCUSSION

Written Discussion: By R. L. Duff, metallurgical technologist, Standard Oil Development Co., Linden, N. J.

The tests reported in this paper are a step in the right direction and the results corroborate some of the theories advanced as to the cause of failure in carbon steel tubes. It has long been felt by many investigators that the carbide formation in steel exerted a marked influence on its physical properties. Until the authors' work was made public little or no test data was available so that controversies on the effect of carbon at elevated temperatures continued.

It is regrettable that the tests reported were not carried out in at least some cases for longer periods of time. The effect of longer heating might be to produce spheroidization at temperatures below 1200 degrees Fahr. (650 degrees Cent.). This theory and a formula taking into account both time and temperature, have been advanced by several metallurgists. If spheroidization does take place at lower temperatures than shown by the authors, then it seems only logical to suppose that little difference in strength or ductility will be found in steel of different carbon content when tested at temperatures of 800 degrees Fahr. (425 degrees Cent.) and above. This is borne out by the results obtained on the Si-Cro-Mo steel.

It is hoped that the authors and others will continue tests of this type as information in this field is badly needed.

Written Discussion: By P. G. McVetty, Research Laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

The authors of this paper have presented more complete information than is usually found in published high temperature test data. By so doing, much

of the uncertainty which accompanies the interpretation of such data is removed and the results are worthy of most careful consideration.

At the present time the question of stability of alloys in service at elevated temperatures is receiving much attention. This has been found necessary because satisfactory operation in service depends upon much more than a knowledge of secondary creep rate determined in a relatively short test. Of particular importance is the study of effect of structural and dimensional changes during the progress of a creep test since they must be considered in any attempt to extrapolate the creep curves.

In comparing the four steels tested it should be noted that the original heat treatments are not quite identical in that the higher carbon alloy steel received a double anneal not given to the other three materials. This would be expected to increase the spheroidization of cementite with a probable decrease in creep resistance.

In a study of this kind much depends upon the accuracy of the assumption that all test specimens of the same material are exactly similar. In comparing tensile properties before and after the creep tests, it would be very valuable to know how much variation existed in the duplicate tests of the original material. This factor is of considerable importance in the interpretation of Table VI.

Evidences of spheroidization are marked after 1100 hours at 1200 degrees Fahr. (650 degrees Cent.) and further changes may be expected after longer exposure. This raises an important question as to whether or not similar changes might have been produced if the heating at 800 and 1000 degrees Fahr. (425-540 degrees Cent.) had been sufficiently prolonged. Bailey and others have found this to be the case and it is probable that some weakening effect of spheroidization should be expected in a long service life at temperatures as low as 800 degrees Fahr. (425 degrees Cent.).

When tests show changes in structure, or tension or impact properties as a result of exposure to stress and temperature during a creep test it is impossible to accept the creep rate measured during the second stage as representative of what the creep rate will be during a service life of many years. Any structural change may be accompanied by a dimensional change more or less independent of the applied stress. This change may either increase or decrease the measured creep rate and it is reasonable to say that the creep curves of Fig. 9 represent the net effect of creep and any dimensional change due to change in structure. Under these conditions it is difficult to predict the slope of the curve if the tests were continued. This condition is characteristic of all creep curves of unstable materials and its effects should not be neglected. When creep rates are plotted against stresses as in Fig. 10 and 11 there is a tendency to assume that the rate is constant over a considerable period of time. In the presence of evidence of lack of stability during the creep test this assumption is seldom justified.

By making these tests, the authors have emphasized the great importance of stability upon the interpretation of all creep tests and it is hoped that others who report creep test data will also study the accompanying structural changes and their effects.

Written Discussion: By L. L. Wyman, General Electric Co. Research Laboratory, Schenectady, N. Y.

Dr. White and his associates are to be congratulated for this further contribution to our too meagre knowledge of the creep of metals at elevated temperatures. The authors have followed the changes taking place in the metals throughout the testing, but I should like to call attention to the effects of variations in the metals before testing.

I am not sure that the following discussion is directly applicable to this present work of Dr. White and his associates, but I do feel that it is a factor of such vital importance as to be called to the attention of all those interested in creep testing.

Briefly, the work at the General Electric Company on creep testing, using in this instance nickel-chromium-molybdenum steels, has shown that the lack of structural uniformity of the steel causes variations in results which far exceed the effects of alloying.

Citing examples of this variation, a structurally uniform steel may show a creep strength of over 35,000 pounds per square inch, while a similar steel when severely banded gives but 11,000 pounds per square inch.

Another instance was where a badly banded steel gave a strength of 12,500 pounds per square inch, while a similar material in the form of a 10-inch billet from a 21-inch ingot showed severe banding in the billet, but this banding was eliminated by a ten to one forging operation, and the resultant structurally uniform bar gave a creep strength of nearly 30,000 pounds per square inch.

Again, ingots of the same composition were cast in such manner as to permit the dendritic growth in the one case, and to restrict it by controlled cooling in the other. The results of this comparison corroborate the above experiments.

It would seem that when such wide variations may be existent, it is rather hazardous to endeavor to analyze a set of creep results in order to evaluate the effect of some alloying material.

For those who may be interested in a more complete description of the experiments noted above, I should refer them to the current issue of Mechanical Engineering Magazine.

Written Discussion: By Dr. C. R. Austin, associate professor of metallurgy, Pennsylvania State College, State College, Pa.

I should like to take the opportunity to record an appreciative comment regarding the use of the microscope in adding to our knowledge of the factors which are important in a study of creep phenomena. At the Pennsylvania State College we are working somewhat along the lines indicated in the authors' paper and we feel that in the past perhaps too much emphasis has been given to the purely engineering phase of the subject. By this I wish to imply that it is eminently desirable to consider in the fullest detail, permitted by experimental technique, the factors which are responsible for the so-called creep rate data we have been accumulating during the past few years.

It is slowly being appreciated that during creep testing the structure of our test samples is gradually but definitely changing and we need to know how and why these modifications are taking place and more particularly the relative importance of the factors which are controlling these changes.

In considering the pearlitic type of steels there seems little question that high creep values are obtained at elevated temperatures when the carbide is

present in a highly dispersed state and that the strength of the steel gradually diminishes as we progressively move toward what is usually spoken of as the spheroidized state. This fact has been nicely brought out by the authors in data presented on the steels which they have studied.

However, it is important that we begin to press the study of the mechanism of these phase aggregations and that we obtain quantitative data on the influence of all factors which we believe instrumental in modifying these changes.

I should now like to make a few references to data and specific comments found in the paper. It is interesting to note the irregularity of the data plotted in Fig. 9. No attempt is made to draw a smooth curve representing the mean position of the elongation-time trace. Do the authors wish to infer that there are true discontinuities in this relationship? Some authorities suggest that creep occurs by successive small steps indicating periodic sudden yielding or slip in the metal, but the discontinuities in Fig. 9 apparently do not represent this phenomenon. Further, does the ordinate-elongation per cent indicate total elongation, that is plastic and elastic, or only the plastic elongation resulting from creep?

The tensile tests were conducted in duplicate but presumably one test had to suffice for the creep data. If the authors have data available on duplicate testing such as that described in the present paper I should welcome some information on reproducibility of data respect to initial deformation and to rate of creep as indicated in Fig. 9.

We have become accustomed to the suggestion that a linear relationship exists between a logarithmic or semi-logarithmic plot of stress and creep rate. In Fig. 11 for DM-45 at 1000 degrees Fahr. (540 degrees Cent.) a definite curvature in the relation is shown whereas in Fig. 10 for Steel 1040 a discontinuity is evident. Does this have any significance?

In discussing, on page 1012, the tensile properties of the steels the authors state that their results might indicate that increased carbon content decreases the stability of pearlitic steels under prolonged heating whereas on page 1014 (last paragraph) it is recorded that carbon content appears to have little influence on the structural stability at elevated temperatures. Since this problem is a vital one in the selection of material subject to stress at elevated temperatures amplification of their views would be welcome.

The paper constitutes a further valuable contribution by the authors to their extended studies of the creep properties of steels at elevated temperatures.

Authors' Closure

Both Messrs. Duff and McVetty have raised a question which is of great importance both from a theoretical and practical standpoint—that is, whether or not structural changes occur in steels at temperatures below 1200 degrees Fahr. (650 degrees Cent.). We have in progress in our laboratories several extended-time creep tests on both plain carbon and Si-Cr-Mo steels at 1000 degrees Fahr. (540 degrees Cent.). One of the plain carbon steel specimens, which was subjected to a stress of 10,000 pounds at 1000 degrees Fahr. (540 degrees Cent.), recently fractured after 3680 hours. The metallographic structures before and after this creep test are shown in the two photomicrographs accompanying this closure (Fig. 1). If these two are compared it will be ob-

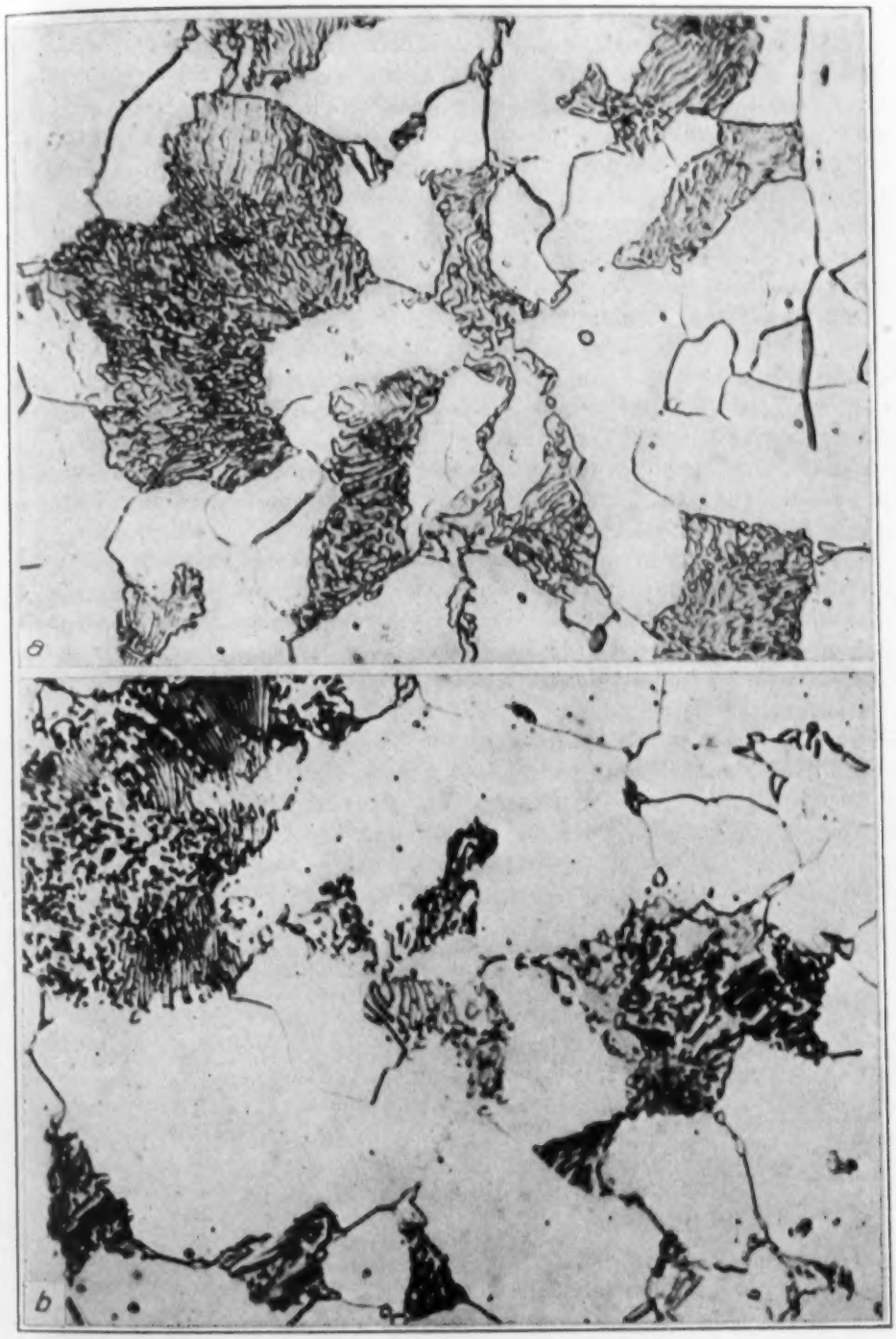


Fig. 1—Metallographic Structures of 1015 Steel (Electric) Before and After a Creep Test at 1000 Degrees Fahr. Under a Stress of 10,000 Pounds. Time for Rupture was 3680 Hours.
(a) Original Structure at 1000 Diameters. Note Laminated Pearlite.
(b) Completed Creep Specimen. Note Partial Spheroidization of Pearlite.

served that while in the original condition the pearlite is largely laminated, after the creep test certain of the pearlitic areas have undergone some spheroidization.

While this would indicate that spheroidization can occur at 1000 degrees Fahr. (540 degrees Cent.) additional results should be obtained before too definite conclusions are drawn. Many more extended tests are in progress and certain of the preliminary results were presented before the A.S.T.M. last June. Certain of these tests have been in progress for 14,000 hours and the loads are so adjusted that fracture will result at periods up to 20,000 hours. The examination of these specimens, upon the completion of the tests, will offer further proof as to the structural stability at 1000 degrees Fahr. (540 degrees Cent.).

The question raised by Mr. McVetty as to the agreement obtained from the tensile tests at room temperature is important in showing the uniformity of the original steels. These results are given in Table I accompanying this reply. The agreement is very good especially in regards to the more common values such as tensile strength, elongation and reduction of area, thus indicating a high degree of uniformity in the steels.

The authors are in agreement with Mr. Wyman's comments concerning the influence of other factors, such as the lack of structural uniformity, on the resulting creep characteristics. We are somewhat surprised, however, at the magnitude of the differences he has observed. A large number of factors have been investigated in our laboratories and while many have been found to have a pronounced influence we have seldom if ever observed differences of over 300 per cent such as Mr. Wyman has quoted. A metallographic examination at 100 diameters has shown these four steels to be relatively free from banding.

Dr. Austin has raised a question as to the smoothness of the time-elongation curves of Fig. 9. Since the elongation or creep is the resultant of two

Table I
Agreement in Tensile Properties at Room Temperature Between Duplicate Specimen of Each of the Four Steels Considered

Steel	Tensile Strength Lb./Sq. In.	Yield Stress (0.2%) Lb./Sq. In.	Proportional Limit Lb./Sq. In.	Elongation % in 2 In.	Reduction of Area %
1015	57,400	33,750	16,000	40.0	67.4
	57,250	34,500	15,750	39.0	67.9
	57,325	34,125	15,875	39.5	67.65
1040	89,300	45,000	32,500	26.0	41.9
	88,400	44,250	32,500	26.0	42.3
	88,850	44,625	32,500	26.0	42.1
Si-Cr-Mo (0.07 C)	66,250	38,000	26,000	37.0	72.7
	66,750	32,400	22,000	36.0	72.7
	66,500	35,200	24,000	36.5	72.7
Si-Cr-Mo (0.48 C)	97,550	45,000	30,000	25.0	49.3
	96,550	45,000	35,000	26.0	48.6
	97,050	45,000	32,500	25.5	48.95

opposing factors, strain-hardening and recrystallization, it is not believed that an entirely regular curve will ever be obtained, especially at temperatures below or only slightly above the lowest temperature of recrystallization or equicohesive temperature. Of course, the magnitude of the irregularities depends upon the sensitivity of plotting but the authors are thoroughly convinced that for studies of this type an extensometer system with a high degree of sensitivity should be used and that the results should be plotted to this same degree of sensitivity.

In further reply to Dr. Austin, it is true that duplicate creep tests were not conducted under the same stress. When the logarithmic method of plotting is used, however, such as in Figs. 10 and 11, and at least four different stresses are employed for determining these curves, it is believed that each test is a check on the other three. Actual duplicate tests have, however, been conducted in many cases. As an example, two tests were recently completed on the same steel at 1000 degrees Fahr. (540 degrees Cent.) under a stress of 7500 pounds. The respective creep rates were 0.028 and 0.031 per cent per 1000 hours and these are believed to be in good agreement. We have found that the final creep rates are more apt to be in agreement than the results obtained during the so-called first stage of creep.

In regard to the comments concerning Fig. 11, it has generally been found that the plotting of stress and the corresponding creep rates to logarithmic coordinates results in a straight-line relationship. Such is not always the case and it is believed that if a sufficient range in creep rates were considered this curve would become asymptotic both at the low and high stress regions. It so happens that the majority of creep tests are conducted in the intermediate range in which the relationship is an approximate straight line.

Dr. Austin also questions certain statements made concerning the influence of carbon content on the high temperature stability. On the basis of the room temperature tensile tests on the completed creep specimens it was found that the creep tests at 1200 degrees Fahr. (650 degrees Cent.) lowered the proportional limit values of the higher carbon steels to a greater degree than those of the lower carbon materials. Since some claim that this value is the only one of the short-time tensile properties apt to prophesy the creep strength to any degree, the statement was made that increased carbon content might lower the high temperature stability. When all factors, such as impact tests and a metallographic examination of the creep specimens as well as the tensile tests, are considered, however, increased carbon content appears to have little influence.

A NEW HEAT RESISTANT ALLOY

By S. L. Hoyt and M. A. Scheil

Abstract

A new heat resisting alloy of iron-chromium-aluminum containing 37.5 per cent chromium and 7.5 per cent aluminum is described. This alloy is melted in the high frequency furnace, and its ingots are rolled to rod or ribbon, or swaged to wire for use in electric furnace resistor elements. On life test and in furnace operation the new alloy has many times the useful life of the standard nickel-chromium alloy. The temperature range for operating the metallic resistor type of electric furnace has thereby been raised to 2300-2400 degrees Fahr. (1260-1320 degrees Cent.). Details of life testing, properties, and behavior are given in the paper.

EARLY work on heat resisting alloys in the metallurgical laboratories of the A. O. Smith Corporation consisted largely of exploratory studies of a wide range of compositions in both major and minor components. A part of this work was devoted to Fe-Cr-Al alloys containing up to 25 per cent aluminum and up to 15 per cent chromium and smaller amounts of other ingredients. As a result of this work U. S. Patent No. 1,990,650 was granted to Dr. Hans Jaeger, then on the staff of the senior author, and assigned to the A. O. Smith Corporation. Latterly our interest has centered on another group of Fe-Cr-Al alloys containing above 35 per cent chromium and 5 per cent aluminum on which U. S. Patent No. 1,995,923 was granted to S. L. Hoyt and R. S. Archer and assigned to the A. O. Smith Corporation. Our alloy No. 10 belongs to this group and contains about 37.5 per cent chromium and 7.5 per cent aluminum. It is this alloy that will be discussed here.

Since the early work of Marsh certain alloys of Fe-Cr-Al have been known to possess resistance to oxidation at high temperatures, though their use has been relatively limited. In this country

---

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. Of the authors, S. L. Hoyt is Director of Metallurgical Research and M. A. Scheil is Research Metallurgist of A. O. Smith Corp., Milwaukee. Manuscript received May 31, 1935.

the two alloys "Alcress" and "Ohmax" have been used to a limited extent while a somewhat similar alloy has been produced in Germany which is known as "Megapyr".[1] In addition to these three ternary alloys, an Fe-Cr-Al-Co alloy which is known as "Kanthal" has been made in Sweden.

The alloy which is discussed in this paper is designated as "Smith Alloy No. 10" and contains exceptionally large amounts of the alloying elements. It will be referred to throughout the paper as "No. 10 alloy." When properly made it has a unique combination of high temperature stability, high melting point, low growth, and good working properties for wrought products. Up to the present the authors' attention has centered on the production of wire and rod for heating elements though some work on castings suggests that there should be important applications of this alloy in that field also.

Manufacturing Procedure

Several different methods have been used to melt the heat resisting alloys of this investigation but the one most commonly relied on was the high frequency induction furnace. Small melts of about 10 pounds were made with a small 20-kilowatt set of the arc gap type while larger melts of about 25 or 165 pounds were made on a 65-kilowatt furnace, run off a motor generator set. At times the melts were cast into long bars about ½ inch in diameter and used in the cast condition for test. Other bars were cast in larger sections, forged to ½-inch square or round, machined to about ⅜-inch round and tested. Ingots were forged into billets or flat slabs and subsequently rolled into strips on a small experimental mill to give material for various tests. At an early stage of this development a No. 2 Torrington swaging machine was installed, after which it was possible to cast alloys as ⅜-inch round bars, and swage them to ¼ or ⅛-inch wire, for test. This latter practice permitted the testing of alloys for behavior in casting, for working properties, and for high temperature stability and is now used as a standard procedure for surveying alloy compositions.

Wire for electric furnace manufacture is made by casting the alloy into ingots and rolling directly (without first forging to billets) to ¼-inch round wire. After the wire has been made, whether it

[1] See "Vacuumschmelze," Heraeus Vacuumschmelze A. G. See also A. Grunert, W. Hessenbruch, and K. Schichtel, "Die Elektrowärme," Jan. 1935.

be for experimental purposes or for furnace construction, it is tested quantitatively for high temperature stability. This property is best estimated for these purposes by means of life tests and this phase of our activities has occupied such an important position that our methods of testing will now be considered in some detail.

Testing Procedure

Preliminary Scaling Tests. A standard test for alloys which are required to be resistant to scaling at high temperature is that of heating test samples in the atmosphere in question under standard conditions. The quality figure is secured by determining the amount of scale which forms per unit time, per unit area, at the particular temperature employed. The amount of this scale can be determined either as the increase in weight if the scale is left intact, or as the loss in weight if the scale is removed. The authors have generally preferred the latter though it is recognized that at times this figure may be misleading due to the inability to remove all of the scale which has formed. This type of test is commonly used for heat resisting alloys and in some instances is about the only one which can be used. In general it is sensitive enough to distinguish between different classes of heat resisting alloys and between the heat resistant alloys and alloys which are not resistant. This method, however, is not as precise nor as satisfactory as the electrical method which is commonly used for resistor materials.

The size and shape of the sample is not critical but we have used blocks about 1 by 3 by ⅛ inch thick or rods ¼ inch in diameter by 6 inches long. Test temperatures from 2200 to 2500 degrees Fahr. (1205-1370 degrees Cent.) have been used because most of the alloys were more than commonly resistant to oxidation. Usually a somewhat lower temperature is used for such tests. Dr. Hans Jaeger found in his work that heat resistant alloys of high quality lose about 0.5, 1.0, and 2 grams per square meter per hour at the temperatures of 2200, 2375 and 2500 degrees Fahr. (1205, 1300, 1370 degrees Cent.) respectively on continuous exposure for six hours. Since then we have standardized on 2400 degrees Fahr. (1315 degrees Cent.) as a suitable test temperature. By utilizing the principle of determining the loss of weight the severity of the test was increased by putting the samples through heating and cooling cycles which permits the scale to snap off on cooling to room temperature.

This type of test was adopted as a standard gas furnace test and is termed the "in and out" test. For the ¼-inch round bars a time cycle of 13 minutes or a 5-minute heating period and an 8-minute cooling period was used. This was long enough to allow the sample to cool to about 200 degrees Fahr. After ten cycles the bars were cleaned of scale and weighed.

The "in and out" test brought out the excellent heat resistance of the standard nickel-chromium alloy with a loss in weight of 10 to 60 grams per square meter per hour whereas pure iron lost over 6000 grams under the same circumstances. An Fe-Al alloy with 6 per cent aluminum showed a loss of 5400 grams to indicate possibly a small improvement but no real resistance to scaling. Good heat resistant alloys showed losses ranging from 10 to 100 grams while the No. 10 alloy showed a loss of only 1.6 grams. The high chromium Fe-Cr alloys showed losses of about 100 grams while the addition of small amounts of other elements lowered this to the order of 25 to 85 grams. Furthermore, the results of the "in and out" test were more consistent and discriminating than the continuous tests. One discrepancy was observed which was the lower loss found with the Ni-Cr alloy than with a number of the Fe-Cr-Al alloys, though this did not hold for the No. 10 alloy.

The "in and out" gas furnace test supplied useful information and it was simple to carry out but it was realized that a more reliable and critical index of alloy quality was required and it was finally abandoned in favor of the electrical life test.

Electrical Life Test. One of the important characteristics of an alloy for use as a metallic resistor is its ability to retain a constant high temperature resistance. This requirement is reflected in the use of the life to a 10 per cent increase in resistance as a criterion of metal quality. Obviously a test which is based solely on the loss in weight does not give a measure of this characteristic, or at the best gives only partial measurement of it. Such effects as intergranular penetration of the deteriorating element and "internal oxidation" are completely missed and even tend to mask the measurement of loss in weight. The formation of visible cracks is another harmful effect which should be evaluated but which is missed by the loss in weight method. Such behavior would be revealed readily enough by an inspection of the test samples if the test has been of long enough duration to bring them out. After all there is a real difference between superficial scaling and high temperature stability and to bring

out the latter characteristics, we turned to the electrical method of testing.

A standard procedure for life testing resistor wires has been considered by the American Society for Testing Materials and is given in their Standard B75-33, "Accelerated Life Test for Metallic Materials for Electric Heating." This is the test of Bash and Harsch and requires no review here, except to point out that a 21 gage wire (diameter of 0.028 inch) is put through two minute heating and cooling cycles at the test temperature of 1950 degrees Fahr. (1065 degrees Cent.). The temperature is periodically checked with an optical pyrometer and is held reasonably constant by maintaining a constant voltage across the wire. The life to a 10 per cent increase in resistance and the life to burn out are used as criteria of the performance. Of these, the former is the more useful because in practice an increase in resistance of more than that amount would usually mean that the proper wattage could no longer be maintained on the furnace.

For the No. 10 alloy it was found necessary to modify the Bash and Harsch test for two reasons. With one or two exceptions the smallest wires that were made were ⅛ inch in diameter and the test temperature of 1950 degrees Fahr. (1065 degrees Cent.) would be so low for these alloys that far too long a time would be required for a test. On one occasion a test on 21 gage wire ran for 2500 hours without reaching a definite end point. This is too long for practical testing. While the principle of the Bash and Harsch test has been retained it has been modified to suit our own conditions. The wire is swaged to 0.125 inch and is tested at some temperature between 2300 and 2600 degrees Fahr. (1260-1425 degrees Cent.). The latter is the standard test temperature. The ⅛-inch wire takes about three minutes to cool to below 212 degrees Fahr. so the cycles are made 3¾ minutes on and off. These cycles are controlled by a telechron clock movement which makes two revolutions per hour and drives a segmented contact disk whose contacts control two clapper switches. Two wires are tested simultaneously, the heating current being sent alternately through the specimens.

Alternating current is used for heating though in the first equipment direct current was used from a motor generator set. In neither case do voltage fluctuations affect the test, due to the photoelectric cell control of the wire temperature. As soon as the current comes on the wire it begins to expand, and in 20 to 25 seconds

the wire reaches the test temperature. This temperature is previously set with the optical pyrometer and the control of the photoelectric cell is so adjusted that it will maintain the temperature set. The actual value of the heating current is set by a rheostat at about 5 per cent in excess of that required to maintain the wire temperature at the test temperature. As soon as the wire temperature rises slightly above the test temperature, the photoelectric control actuates a relay which cuts in a small auxiliary resistance and lowers the current by about 10 per cent. This allows the wire temperature to fall slightly below the test temperature whereupon the photoelectric cell again functions and cuts out the auxiliary resistance to repeat the cycle. The amount of the auxiliary resistance can be varied by a rheostat. This is usually adjusted so that the relay operates on a two to three second period. Increasing the actual current by means of the main rheostat does not raise the temperature of the wire above the test temperature and has the effect only of increasing the rapidity with which the relay works. The temperature variations above and below the temperature for which the wire is set are very small. A variation of not over 2 milliamperes is observed with the optical pyrometer during the operation of the relay and this means that the surface temperature must be constant to about 10 to 15 degrees Fahr. during one cycle.

Recent studies upon the expansion of heated wires in the life tester show that the heated wire contracts 0.004 inches when the auxiliary resistance is cut in. Converted to degrees Fahr. this contraction amounts to a decrease of about 30 degrees Fahr. Upon increasing the current to 15 per cent above that required to hold the wire at the test temperature, the expansion measurements show that the wire is heated 15 degrees Fahr. above the test temperature. This would be an extreme case as we usually use a current which is only 5 per cent above that necessary to hold the wire at the test temperature. While the expansion measurements would indicate that temperature variations are in excess of 1 per cent of the test temperature (about 1.25 per cent at 2400 degrees Fahr.) the optical pyrometer measurements indicate that the surface temperature varies less than 1 per cent of the test temperature (about 0.4 to 0.06 per cent at 2400 degrees Fahr.). The explanation of this discrepancy between the two methods of measuring the temperature variations is that the internal and surface temperatures probably respond at different rates when the auxiliary resistance is cut in or out.

Over long periods of time it was found that the photoelectric cell maintains the temperature of the wire accurately, or well within a 1 per cent variation. In a test which ran 2500 hours the only adjustments which were required were made during the first 300 hours. At the start of a life test at temperatures of 2300 degrees Fahr. (1260 degrees Cent.) and above on 8-gage wire it is necessary to check the temperature after the first three hours. During this time the oxide coating is developing and the emissivity of the surface is changing, while the temperature rises slowly until the surface reaches a constant emissity. After this the wire temperature does not change unless the relative position of the wire with respect to the photoelectric cell is changed, such as would be caused by growth or sagging. By keeping the wire straight at all times during test the photoelectric cell maintains a constant temperature.

An ammeter and voltmeter are used to determine the hot resistance of the wire after the aging period and throughout life, and it is the increase in resistance that is used as the criterion of performance. When taking these measurements the auxiliary resistance is adjusted so that the photoelectric cell controls slowly. This holds the current constant for a sufficient length of time to make good readings. Each time such a resistance measurement is made the wire temperature is also determined for record. In addition we have a recording ammeter in series with the test wires to give a complete life history of each wire even though the burn-out occurs at night or over the week end.

The aging period used in testing Alloy No. 10 at temperatures above 2300 degrees Fahr. (1260 degrees Cent.) has been 10 minutes. This phase of life testing has not been thoroughly investigated although a uniform high temperature aging treatment should tend to give more uniform results regardless of the test temperature. With the usual procedure a relatively rapid increase in hot resistance during the first 4 to 50 hours, is obtained depending on the test temperature. This increase is of the order of about 2 to 3 per cent in ten hours. After this, the hot resistance rises slowly with increase in time.

The disappearing filament optical pyrometer was used to determine the apparent surface temperatures of the wires heated in the open. The pyrometer was standardized to read black body temperatures (BBT) and the observed surface temperatures of the heated wires are recorded as black body temperatures. The true surface

temperature must be obtained by adding a correction for emissivity. The pyrometer was standardized by comparison with a 3-millimeter wide tungsten ribbon filament lamp supplied with calibration by the Lamp Development Laboratories of General Electric Company, Nela Park, Cleveland, Ohio.

Life Test Results

The observations made during a test cover the following points:

(1) *Increase in resistance with time.* In conformance with practice the useful life of the wire is taken arbitrarily as its life to a 10 per cent increase in hot resistance. That is the chief use of this information. At the start resistance readings are taken after 1 hour, 3 hours and 9 hours. From then on readings are taken twice daily at intervals of 9 and 15 hours. After about 24 hours of life testing the increase in resistance up to that time gives a fair idea of what performance may be expected. At 2600 degrees Fahr. (1425 degrees Cent.) if the resistance increases more than 5 per cent after 24 hours, the life of the alloy will usually be less than 50 hours, while if the increase is much less than 5 per cent or about 3 to 3.5 per cent then the life will be in excess of 80 hours to a 10 per cent increase.

The characteristics of No. 10 alloy in respect to resistance changes at temperatures of 2300 degrees Fahr. (1260 degrees Cent.) and above are different than those found with the Ni-Cr alloys. After the first rise, the resistance increases uniformly and slowly with time, the only difference between low and high life testing temperatures being in the rate of resistance increase. The Ni-Cr alloy shows a very small change at the start and at a later period shows a relatively rapid rate of increase in resistance.

(2) *The sag or growth of the wire.* Heated wires of the Fe-Cr-Al alloys do not remain straight during life test at high temperatures but tend to bow out and sag near the bottom copper contact. This occurs even when heated with no load on the wire. By adjusting the weight on the counterbalance of the lever arm supporting the bottom copper contact, the heated wire can be maintained straight during life test. The growth of the vertically suspended wire can be measured and the suspension distance changed to compensate for the growth. Our present practice is to adjust the weight on the lever arm to produce no load on the wire, and in this way to avoid the effects of creep. The measurements of the increase in length are made in 1/1000 inch and are recorded with the resistance measure-

ments to give the growth in per cent. It is believed that these measurements give an index of the dimensional changes that may be expected to occur in a furnace by prolonged heating of the elements. In the Bash and Harsch test a load of about 35 pounds per square inch is suspended on the wire during test. It would also be possible to maintain a load on the wire with our test but we have thought it better at the present to eliminate creep.

(3) *The development of "hot spots."* Like all other metallic resistors after the wire has been on test for a period of time it is

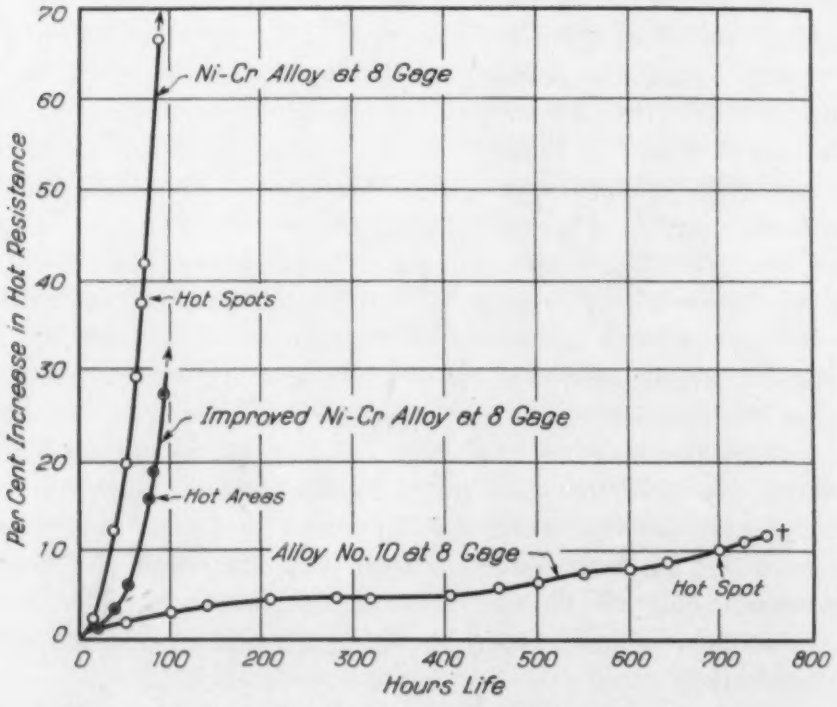


Fig. 1—Life Tests at 2300 Degrees Fahr. (1260 Degrees Cent.).

observed that certain portions of its length show a brighter color on heating than the rest of the wire. At a later period these hot spots are found to be running at a higher temperature than the rest of the wire. This produces a run-away condition and the wire burns out shortly thereafter.

It is naturally of great interest to compare the results obtained with No. 10 alloy with those obtained with commercial samples of resistor wire. For the latter the 80 per cent Ni - 20 per cent Cr alloy has been used. The curves of Fig. 1 show the results obtained with two samples or the Ni-Cr alloy and one sample of No. 10 alloy,

all being ⅛ inch in diameter. One of the former is an improvement on the other and this is clearly brought out by the life test. The resistance of the Ni-Cr alloy increases at a slow rate at the start but suddenly rises quite rapidly in our tests. Standard practice would dictate the use of the 10 per cent life as a criterion of excellence of this alloy but it would appear to be more appropriate to use the life at which the resistance commences to rise rapidly. The No. 10 alloy shows a gradual rise in resistance and reaches its 10 per cent life at about 700 hours, as compared to the life of 55 or 65 hours for the improved Ni-Cr alloy, depending on which point is taken. The test temperature in this case was 2300 degrees Fahr. (1260 degrees Cent.), that being the black body temperature of each wire uncorrected for emissivity. This temperature appears from other considerations to be suited to a direct comparison of these wires, though it does require a long time for tests on No. 10 alloy. To avoid tying up the testing equipment for such long periods 2600 degrees Fahr. (BBT) was selected as a suitable test temperature for this alloy.

In selecting the test temperature it was felt that it should be set high enough to reduce the time of testing to a reasonable length but not so high that extraneous factors would be thereby introduced which would militate against securing reliable and reproducible data. The Ni-Cr alloy was tried out at 2300, 2400 and 2500 degrees Fahr. (BBT) (1260, 1315, 1370 degrees Cent.). At the latter temperature the results were erratic and the life was much shorter than would be predicted by tests at lower temperatures. This introduces us to an important point and we may well consider, at this place, the effect of temperature on the life of the wire.

Effect of Temperature on Life

A brief consideration of the phenomena which must be responsible for the deterioration of the wire made it appear likely that the relation between life and temperature would be exponential, or in other words that this relation would be expressed as a straight line if the data were plotted as the log of the life versus the reciprocal of the absolute temperature. Various pertinent data were secured from the literature and when plotted in this way this assumption was found to be a correct one. Many subsequently performed tests have confirmed this viewpoint and the relation seems to be a truly straight line over quite a range in temperature. Obvi-

ously this relation can now be used to estimate the life at any temperature over the range for which it holds. When one estimates, in this manner, the expected life of the Ni-Cr alloy at 2500 degrees Fahr. (1370 degrees Cent.) on the basis of its life at 2300 degrees Fahr. (1260 degrees Cent.) it comes of the order of 10 hours. The actual life was found to be of the order of only two hours which shows that some additional factor enters to affect the results. The melting point of the Ni-Cr alloy is known to be about 2550 degrees Fahr. (1400 degrees Cent.) and if we apply a correction for emissivity it is clear that at 2500 degrees Fahr. (BBT) (1370 degrees Cent.) the wire is too close to the melting point for testing

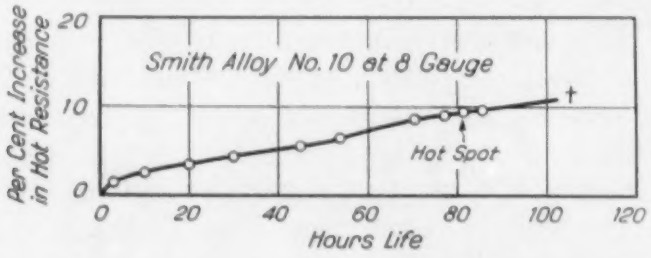


Fig. 2—Life Test of Alloy No. 10 at 2600 Degrees Fahr. (1425 Degrees Cent.).

purposes. In regard to the No. 10 alloy a similar situation was found at a test temperature of 2650 degrees Fahr. (BBT) (1455 degrees Cent.) and presumably for the same reason. Upon applying a correction for emissivity of 0.5 (according to advice from the Bureau of Standards for this type of surface) the wire of No. 10 alloy was actually operating with a surface temperature of 2830 degrees Fahr. (1555 degrees Cent.). According to determinations of the temperature of incipient fusion which were made by Dr. L. Reeve, formerly of this laboratory, and Mr. Scheil, this point was returned as 2830 degrees Fahr. (1555 degrees Cent.). Using black body conditions which gave true temperatures directly, they found it necessary to heat to above this temperature to produce incipient fusion. Here again a test temperature of 2650 degrees Fahr. (1455 degrees Cent.) would be too near the freezing point of the alloy for reliable results. As against a predicted life of 50 hours, the wire actually failed in about 10 hours or less. When one recalls the true temperature of the wire during this test, that was a noteworthy performance for the wire must have been above the melting point of pure iron, 2785 degrees Fahr. (1530 degrees Cent.) From all

this it appears reasonable to use 2600 degrees Fahr. (1425 degrees Cent.) as the highest practical test temperature for No. 10 alloy. The results secured are compatible with those secured at lower test temperatures and the whole test is completed in about 3 to 5 days. The curve of Fig. 2 reproduces the life test of a wire of No. 10 alloy at 2600 degrees Fahr. (BBT) (1425 degrees Cent.). This test is the standard test to control the quality of heats of this alloy.

The data reported here relate to accelerated life tests and particularly to direct comparisons between the No. 10 alloy and the Ni-Cr alloy. In actual furnace operations the heating elements carry much smaller currents and last much longer than the hours of life shown on life test and it has been our experience that the superiority of alloy No. 10 is repeated in actual furnace operation.

Properties of No. 10 Alloy

The ability of No. 10 alloy to be cast has already been mentioned. Many ingots have already been cast of this alloy and in this work it has been found possible to produce ingots which are smooth on the surface, sound at the center, and with a negligible amount of pipe. This has not been because it is an easy alloy to handle in the foundry but, rather, in spite of some undesirable characteristics. Consecutive analyses and life tests of a series of heats and grab samples of others have shown that it is entirely possible to set up a standard procedure for melting and pouring which maintains the required composition and high temperature stability. The composition comes fairly close to 37.5 per cent Cr and 7.5 per cent Al, and on life test the 10 per cent life comes of the order of 70 to 80 hours at 2600 degrees Fahr. (1425 degrees Cent.) with a burn-out life of about 100 hours.

This alloy is of the type of a severely over-killed steel and is deep piping. Adequate measures must be taken to eliminate the pipe or else to throw the shrinkage to a position where it will do little or no harm.

Ingots of this alloy can be readily forged and at one time a small amount of forging was considered to be good practice to break up the ingot structure. Later it developed that cogging was not only unnecessary but that folds and laps were apt to be hammered into the surface. Being a non-scaling alloy forging could not be relied upon to remove such surface defects. The forging temperatures used were

in the neighborhood of 2350-2450 degrees Fahr. (1290-1345 degrees Cent.) and the billets were returned to the furnace as soon as the temperature fell to about 2100 degrees Fahr. (1150 degrees Cent.) The use of forging is now chiefly in the preparation of test samples for life test. Ingots of this alloy should be heated slowly to avoid heat checks. Ingots about 3½ inches square are placed in a cold furnace and heated slowly in four hours to 2400 degrees Fahr. (1315 degrees Cent.).

The practice for making wire is to roll the ingots directly to billets, condition the surfaces, and finish roll to wire, as has been mentioned. At elevated temperatures the alloy is highly ductile and can be rolled, even with the original ingot structure, with no difficulty. The rods should be finished at about 1700 degrees Fahr. (925 degrees Cent.) and if they are finished at lower temperatures we prefer to anneal them prior to giving them a subsequent treatment. As far as breakage goes the rods can be finished as low as about 1200 degrees Fahr. (650 degrees Cent.) without checking. At room temperature the alloy is brittle.

The electrical resistance of No. 10 alloy is about 1000 ohms per circular mil foot, or about 50 per cent greater than the Ni-Cr alloy. We consider this to be an advantage for it means that this alloy permits the use of larger cross sections or a higher voltage, or some desirable combination of the two. Having had occasion to substitute No. 10 alloy for a Ni-Cr heating element in furnaces it has been found that this can be readily done by the simple expedient of making the cross section 50 per cent greater. In general this is not a satisfactory procedure because the refractories and insulation, and possibly the element supports, are generally not suited to the higher temperatures which can be produced with this alloy.

The resistance of the swaged wire increases with rise in temperature until a maximum (ca. 1200 ohms) is passed through at about 1700 degrees Fahr. (925 degrees Cent.) whereupon it falls with further increase in temperature and reaches a value which at 2600 degrees Fahr. (1425 degrees Cent.) is about 5 to 7 per cent greater than at room temperature. These temperatures are, again, black body temperatures in air without correction for emissivity. This maximum disappears gradually upon heating and after aging for 5 hours at 2600 degrees Fahr. (1425 degrees Cent.) in the life tests, No. 10 alloy shows a maximum deviation of about 2 per cent from the room temperature resistivity of 1000 ohms per circular

mil foot over the temperature range of 1400 - 2600 degrees Fahr. (760 - 1425 degrees Cent.).

The low density of No. 10 alloy of 6.9 grams per cubic centimeter reflects the high aluminum content. Its volume is 22 per cent greater than the volume of an equal weight of the standard Ni-Cr alloy.

The expansion of No. 10 alloy on heating is closely that of the Ni-Cr alloys or about 18×10^{-6} in. per in. per degree Cent. (10×10^{-6} per degree Fahr.) between room temperature and 2400 degrees Fahr. (BBT) (1315 degrees Cent.). This means an expansion of about 0.27 inch per foot, on heating to 2400 degrees Fahr. (1315 degrees Cent.). These determinations were made on wire in the life tester with the Ames dial and are subject to a minor correction when more accurate determinations become available. The growth of the wire on life test and in furnace operation has been mentioned. An allowance for growth of at least ¼ inch per ft. should be made, as well as for the expansion. These characteristics, and any creep or sagging, are accentuated by the extra high temperatures at which furnaces wound with this alloy operate.

Hardness of No. 10 Alloy

The hardness of No. 10 alloy has not been investigated greatly but the following figures will indicate about what degree of hardness it possesses.

	Coarse-grained Ingot	Fine-grained Ingot
Brinell Hardness Number	200	235
Rockwell B	98	100
Ditto, taken in Brinell Impression	110	111
Rockwell C	18	21
Ditto, taken in Brinell Impression	36	40

Grinding and Machining

No. 10 alloy has a low thermal conductivity and a relatively large coefficient of expansion, as a consequence of which relatively large temperature differences must be set up when the metal is ground on the ordinary wheel. The alloy does not easily take a permanent set and hence these stresses are liable to produce heat checks on grinding. On this account the alloy is not ground except under exceptional circumstances or unless the material has been

worked to a fine size. This same combination of properties makes it hazardous to heat large masses of the alloy except at relatively slow rates, or in the same manner as many other heat sensitive alloys have to be heated. Again this sensitivity is not noticed in the small sizes used for furnace construction.

No. 10 alloy can be readily machined by the proper methods, chiefly by milling and turning. A good milling machine with the proper cutter and a generous supply of coolant is capable of machining the alloy with little tool wear. A creditable job can also be done on the lathe, which is the procedure that was used to produce ⅜-inch bars for swaging. So far little success has resulted with a shaper, the principal difficulty being an extremely short tool life. This does not seem to be associated with the tool material used. The usual high speed steel milling cutter was used on the milling machine. Apparently this alloy generates an extra large amount of heat when being machined and this heat must be taken care of if tool failure is to be avoided.

Welding No. 10 Alloy

No. 10 alloy is readily welded with the oxyacetylene torch. It is important to keep the flame oxidizing and not to allow the metal to take up carbon by using an excess of gas. A filler rod of the same alloy is used in the form of ⅛ inch wire. Possibly the oxy-hydrogen torch would be much better but this has not been tried yet. The atomic hydrogen torch has been tried and found to work quite satisfactorily, though experience here has been limited. With both types of welding it has been necessary to use a flux to permit the metal to flow properly and for this a flux of 1 part KCl and 1 part CaF_2 has been found to be satisfactory. This flux cleanses the surface of aluminum oxide which forms and on account of this behavior it is necessary to remove the flux prior to the service of the resistor. After welding, the joint is left in a brittle condition though not necessarily weak. By heating to a red heat the welded joint may be bent or shaped.

Microstructure of No. 10 Alloy

Samples are prepared for microscopic examination by the usual procedure of the metallographic laboratory. The ordinary etching reagents do not attack the alloy though acid ferric chloride does pro-

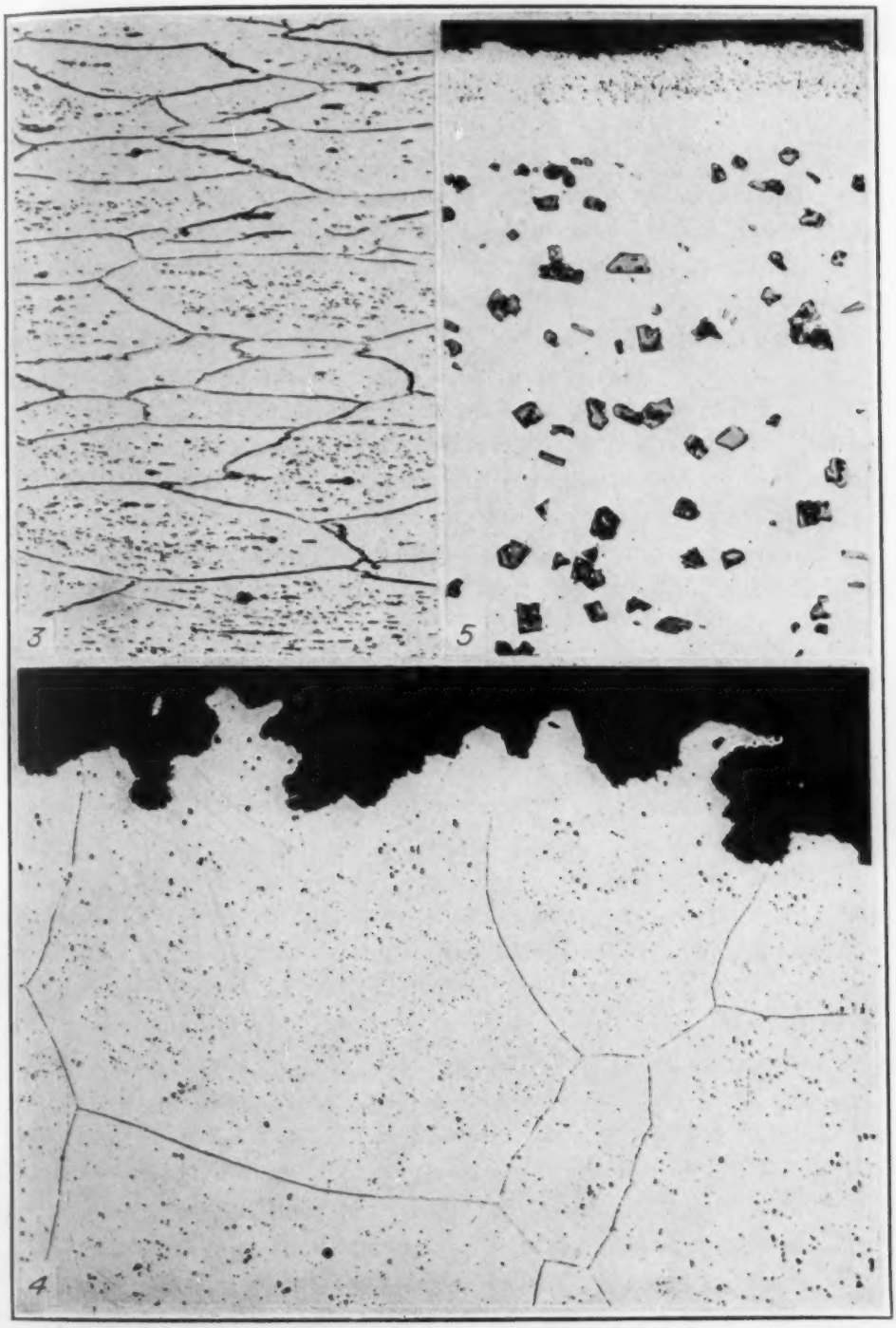


Fig. 3—Photomicrograph of Swaged Wire of Alloy No. 10. × 100.
Fig. 4—Photomicrograph of Wire of Alloy No. 10 After Heating Over 100 Hours at 2600 Degrees Fahr. (1425 Degrees Cent.) Showing Section at Surface. × 100.
Fig. 5—Iron-Chromium-Aluminum Alloy Wire Showing "Internal Oxidation" Below the Surface. × 100.

duce an etch. Warm 40 per cent sulphuric acid has been found to be suited to the development of the structure.

The rolled and swaged alloy is exceptionally free from the coarser oxide inclusions while the etched structure resembles that of alpha iron with a small amount of carbide. Heating produces a recrystallization and continued heating soon produces a stable structure which remains essentially fine-grained throughout life. The swaged wire is shown in Fig. 3 and the wire after burnout at 2600 degrees Fahr. (1425 degrees Cent.) is shown in Fig. 4. The latter photograph shows the edge of the wire with its roughened surface. This photograph also shows that there is no oxygen penetration along grain boundaries, or "internal oxidation." This latter effect is shown for another, and defective, wire of different alloy composition, in Fig. 5. It appears that oxygen has diffused into the interior of this wire, there to be precipitated out as a complex spinel. These crystals are transparent and birefringent with reflected polarized light. This effect has been described elsewhere[3] and we shall not describe it here.

Acknowledgment

Sincere appreciation is extended to our associates who assisted in this development, and particularly to the following: Mr. R. S. Archer, under whose direction this work was begun; Mr. Arthur T. Clarage and Columbia Tool Steel Company for their co-operation in rolling certain of the experimental billets; Mr. A. L. Marsh and others of Hoskins Manufacturing Company for additional assistance in rolling ingots and billets; Mr. B. L. Benbow and others of the Cleveland Wire Works of General Electric Company for assistance in swaging and drawing these alloys; Hevi Duty Electric Company for their helpful advice and many practical tests that they assisted in; Messrs. C. W. Greenidge, M. A. Matush, J. Hunter, and R. G. Johnson of our organization whose skill in carrying out the melting, molding and forging was of inestimable value and to Dr. J. J. Thompson who developed reliable methods of chemical analysis for this type of alloy.

[3]S. L. Hoyt and M. A. Scheil. *Metals Technology*, American Institute of Mining and Metallurgical Engineers, Sept. 1934, Tech. Pub. 567.

DISCUSSION

Written Discussion: By Fred P. Peters, chemist, Wilbur B. Driver Co., Newark, N. J.

The authors and their associates are indeed to be complimented on the development of the alloy described in their paper. Electrical heating methods, on their own merits, are constantly increasing in application, enhancing thereby the industrial importance of the alloys customarily used as resistor material. The introduction of new alloys to resist even higher temperatures must certainly expand the field of electrical heating application still further.

In this respect, it is unfortunate that the authors did not effect a comparison of No. 10 Alloy with materials engineered and marketed for service in a similar temperature range, i.e., 2100 to 2600 degrees Fahr. (1150 to 1425 degrees Cent.) rather than with the nickel-chromium alloy. Admittedly, nickel-chromium alloy is the "standard" resistor material, but it is not at all standard for service at temperatures in excess of 2100 degrees Fahr. (1150 degrees Cent.), which destroy it rapidly. In other respects nickel-chromium alloy and alloy No. 10 are not strictly comparable, as the extremely low cold deformability of the latter eliminates it from consideration for those hundreds of electrical heating applications that require a ductile resistor material in much finer sizes of wire than 8 gage. It would seem that an interesting comparison might be that between No. 10 Alloy and the other iron-chromium-aluminum or the iron-chromium-aluminum-cobalt alloys that the authors mentioned. It is largely alloys of these types, rather than nickel-chromium alloys, that No. 10 Alloy may replace in industrial service at the extremely high temperatures.

Factors other than oxidation-resistance also are essential to the successful application of metallic resistor materials. As a group the iron-chromium-aluminum alloys, in spite of superior oxidation resistance, have found only limited application, because of their pronounced susceptibility to growth, sagging, and brittleness after long heating in the upper temperature ranges. The natural assumption is that No. 10 Alloy also would be heir to these unfortunate sources of failure, although to a lesser degree, because of its much greater alloying content. Whether or not this is so has not been clearly shown by the authors, quite probably and properly because this particular investigation was meant to be concerned only with the oxidation-resistant quality of the new alloy. It is to be hoped that in a later investigation Dr. Hoyt and Mr. Scheil may study the high temperature performance of No. 10 Alloy under conditions more closely approximating those of actual service, i.e., with a nominal tension or load on the specimen during test, and possibly under "constant voltage" conditions rather than "constant temperature." "Constant temperature" tests are excellent for purposes of purely scientific investigation, but as an evaluation of service performance, some doubt exists as to their merit as compared with the "constant voltage" type. Once "hot spots" have begun to develop on the specimen it becomes difficult to measure and maintain the temperature, even with such an ingenious controlling mechanism as the authors have described.

Alloys of this type, less ductile than, but superior in oxidation-resistance to nickel-chromium alloys are of a distinctly different nature all around. Possibly what is most needed in this respect is the development of a "standard" life-test procedure for heavy gage, very high temperature producing materials,

more suited to an evaluation of their properties than is the Bash and Harsch test, designed as it is for the testing of finer wire, and of materials capable of operating at temperatures no higher than 2100 degrees Fahr. (1150 degrees Cent.). Although such development is definitely the province of the American Society for Testing Materials, I mention it here because the authors' investigation has revealed the need for such a test, and because the particular set-up that they used, with certain modifications, should form an excellent foundation for a standardized procedure of this nature.

Written Discussion: By Harold E. Koch, vice-president, Hevi Duty Electric Co., Milwaukee.

In reviewing the paper presented by Dr. Hoyt and Mr. Scheil, we recognize that the development they describe is one which will undoubtedly have a far reaching effect not only on the electric resistance furnace business, but on process work above 2000 degrees Fahr. (1095 degrees Cent.) in many industries. Most of the laboratory furnaces using the present day nickel-chromium heating elements have been limited in operation to temperatures of 2000 degrees Fahr. (1095 degrees Cent.) and there has been very little equipment available at reasonable prices which would lend itself to process investigation above that range.

The use of Alloy No. 10 in laboratory furnaces and its related industrial application is a direct step toward a remedy of this situation. When we couple with the ability of this new alloy to withstand elevated temperatures the fact that electric heat moves into a field in which its operating costs are very definitely in line with low priced fuels, we recognize that the authors have presented a work of major importance not only to the process industries, but to the electrical industry in general.

The course of development of the chromium-iron-aluminum alloys has not been an easy one. From an intimate contact which we have had with the authors and their staff during the progress of this development, we are frank to say we marvelled at the versatility they displayed in breaking down the problems encountered to straightforward metallurgical analysis and in setting up at the same time, melting practices which would assure uniform and consistent results.

The authors are to be congratulated for an excellent piece of work.

Written Discussion: By L. H. Waldrip, engineer, C. O. Jelliff Mfg. Corp., Southport, Conn.

In Dr. Hoyt's paper and particularly in the subsequent discussion, frequent references have been made to an iron-chromium-aluminum-cobalt alloy and the authors have produced laboratory evidence tending to show poor results for this class of alloy at high temperatures. The alloy referred to is known as KANTHAL, which is made in three grades for operation at various temperatures, and we assume that the data produced is for the highest grade, with a maximum recommended operating temperature of 2460 degrees Fahr. (1350 degrees Cent.).

The tables and graphs shown by Dr. Hoyt seem to indicate comparatively short life at high temperatures, marked increase in resistance throughout the useful life, a melting point below that of iron, excessive growth at high temperature and low mechanical strength. It should be pointed out that the normal testing temperature selected by Dr. Hoyt is 2600 degrees Fahr. (1425

degrees Cent.) which is somewhat above the maximum recommended operating temperature for KANTHAL, and at that temperature the results obtained are quite logically considerably different than at normal operating temperatures. Laboratory investigations of KANTHAL have been conducted in Europe for several years, and it is sufficient to say that other investigators' results are somewhat different, particularly with reference to the melting point—but this can probably be traced to the difference in testing methods used.

Strangely enough, alloys of iron-chromium and aluminum, somewhat similar to the Alloy No. 10, have been known and used to some extent in the industrial countries of Europe for several years. Laboratory tests of this class of alloys seem to indicate that they are ideal for high resistance work at high temperature, and several companies in Germany particularly have attempted to market them. However, in practical work there has been difficulty in fabricating the alloy, due to its brittleness.

The only commercial shapes available in the iron-chromium and aluminum alloy to date, as far as is generally known, have been round wires and rods of a fairly heavy section, and they have necessarily been swaged rather than cold drawn or cold-rolled. This limits practical use of the alloy to those element types where a straight wire can be used, or the wire bent around a large radius while hot. Flat strip has not been available. Due to the method of manufacturing, reports are that it has been found difficult to obtain uniformity of the alloy, either in diameter or in resistivity from one lot to another.

On the other hand, the iron-chromium-aluminum-cobalt alloys to which Dr. Hoyt refers, have enjoyed a remarkable increase in use. They were first developed some ten years ago, and after a period of five years were put into practical use, first in industrial furnaces where it was found possible to operate at an element temperature up to 2460 degrees Fahr. (1350 degrees Cent.) with a satisfactorily long life. The alloys are not recommended for operation above this temperature, and any testing that may be done at 2600 degrees Fahr. (1425 degrees Cent.) will show results which are quite different from those obtained at the recommended temperature. There are a large number of European installations which have been in service for from three to five years, ranging in size from very small metal-melting furnaces and laboratory furnaces up to one of a capacity of 900 KW.

Combined with the heat resisting qualities of KANTHAL, is a ductility which is quite similar to the familiar nickel-chromium alloys. It is easily cold drawn into wires as small as 0.005-inch diameter, and cold-rolled to any desirable dimension of ribbon or strip, and the forming of spirals or corrugated strips is generally done in a cold state, except in quite heavy sizes. As a result of long experience the alloys are now made to close limits of uniformity of resistance and life, and the characteristics of one lot can easily be reproduced in the next.

The mechanical properties at high temperatures are quite similar to those of Alloy No. 10 to the extent that both must be well supported in order to produce satisfactory results. Hanging elements are not suitable, and especially at high temperatures a good grade of refractory is essential.

The acceptance of the iron-chromium-aluminum-cobalt alloys in Europe five years ago, and their increased use since then are sufficient proof of their

ability to give good service for the generation of electric heat at high temperatures in all kinds of apparatus from a gold melting furnace or an electric stove element to a large steel treating furnace.

Dr. Hoyt's paper shows the remarkable results for the Alloy No. 10 in the laboratory, but he has not reported any commercial applications where this material has proven successful.

Oral Discussion

L. H. KNAPP:[1] I would like to ask Dr. Hoyt how serious is the problem of growth in this particular alloy when it is operated at temperatures up to 2400 degrees Fahr. (1315 degrees Cent.). I would also like to ask Dr. Hoyt if he feels at the present time that his alloy can be recommended for heat treating high speed steel at that temperature.

Authors' Reply to Discussion

Mr. Peters has raised some very pertinent questions. One of the main points I refer to in this connection is that we correlated the behavior of Alloy No. 10 with that of the standard nickel-chromium alloy, while it would be more to the point if we compared Alloy No. 10 with alloys which more closely approximate its composition, characteristics, etc., and particularly which are designed for use at the high temperatures where Alloy No. 10 is used.

I think I do not need to go into the reason for taking the course that we did in the paper. The nickel-chromium alloy is the standard, and we demonstrated at least to our own satisfaction that it can be satisfactorily life-tested at 2300 degrees Fahr. (1260 degrees Cent.). Anybody who is familiar with the nickel-chromium alloy can draw his own conclusion as to the performance of other types of alloys by simply correlating with the nickel-chromium alloy. However, I realize that it would be advantageous to compare Alloy No. 10 with such other alloys and we have a few figures on that point.

Fig. A shows the growth of three alloys tested in life test under identical conditions, and therefore directly comparable. Alloy No. 10 is at the bottom and shows small growth. The figure has been given in the paper. An alloy of another analysis of iron-chromium and aluminum is No. 2, which shows greater growth than No. 10. Alloy No. 1 is an iron-chromium-aluminum-cobalt alloy also shows greater growth under the conditions of our life testing procedure. It has been our experience that Alloy No. 10 has a low growth when one considers the analysis and the high temperatures to which it is heated.

Fig. B shows a direct comparison on life test. We have found from the semi-logarithmic relationship correlating life and test temperature that the data fall on a straight line so that we can make comparisons at any temperature for which the wire responds properly to life test. Alloy No. 10 in this case shows about twice the life that it did at 2600 degrees Fahr. (1425 degrees Cent.). At the same temperature and under the same conditions, the alloy of iron-chromium-aluminum and cobalt shows the results in curve I.

In reference to the melting point we think that it is unique in that while Alloy No. 10 is an iron base alloy, its solidus or temperature of beginning

[1]Hartford Electric Light Co., Hartford, Conn.

fusion is actually above the melting point of iron. The results of a rather carefully conducted series of tests on this particular point are given in the paper, but for purposes of discussion we are using Fig. C. What we did here was to put a piece of pure iron wire and a piece of Alloy No. 10 wire, both ⅛ inch in diameter, in an alundum boat and then placed the boat at the center of a hydrogen furnace. The temperature was then raised until the iron wire melted down. At the same time pyrometer measurements were made on the

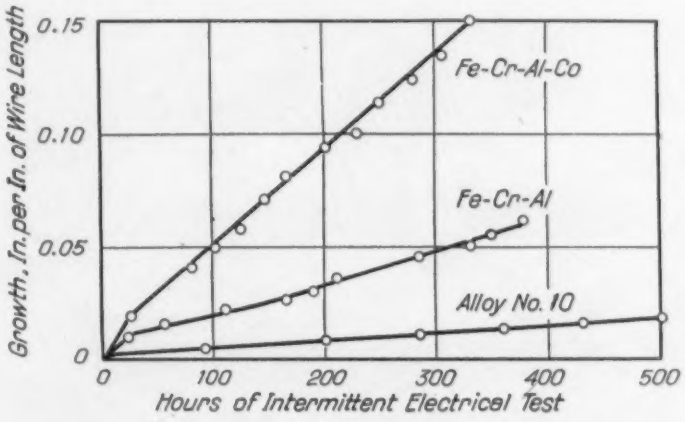


Fig. A—Growth of Three Alloys Tested at 2400 Degrees Fahr. B.B.T. Vertical Suspension—No Load.

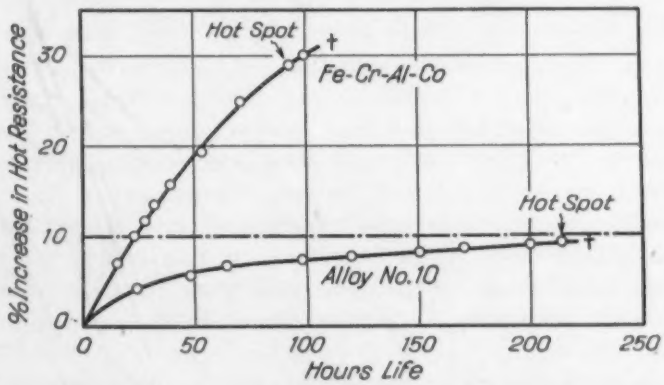


Fig. B—Life Test at 2500 Degrees Fahr. B.B.T. 8-Gage Wire. Cycle 3.75 Minutes Heating and 3.75 Minutes Cooling.

wires themselves. The center figure shows what happened. On the right we see that the iron wire has fused completely, while the temperature recorded by the pyrometer was 2760 degrees Fahr. (1515 degrees Cent.) The true melting point of iron is 2785 degrees Fahr. (1530 degrees Cent.). It will be noted Alloy No. 10 wire is at the left and it has not been affected by the temperature of the melting point of the iron. In the second test we repeated the same procedure except this time we went above the melting point of iron until the Alloy No. 10 specimen went over. The temperature recorded was 2820 degrees Fahr. (1550 degrees Cent.). This work gave a fairly good calibra-

tion of the pyrometer by means of the iron wire. To carry our studies further we used a lower iron-chromium-aluminum alloy with cobalt, an iron wire, and a wire of No. 10 alloy, and put all three in the furnace as before. The first alloy is shown at the right. It began to fuse before the pure iron. The temperature was 2740 degrees Fahr. (1505 degrees Cent.).

Mr. Peters takes up such matters as growth, sagging, and others which relate to furnace operation. We have shown data on growth but we have no

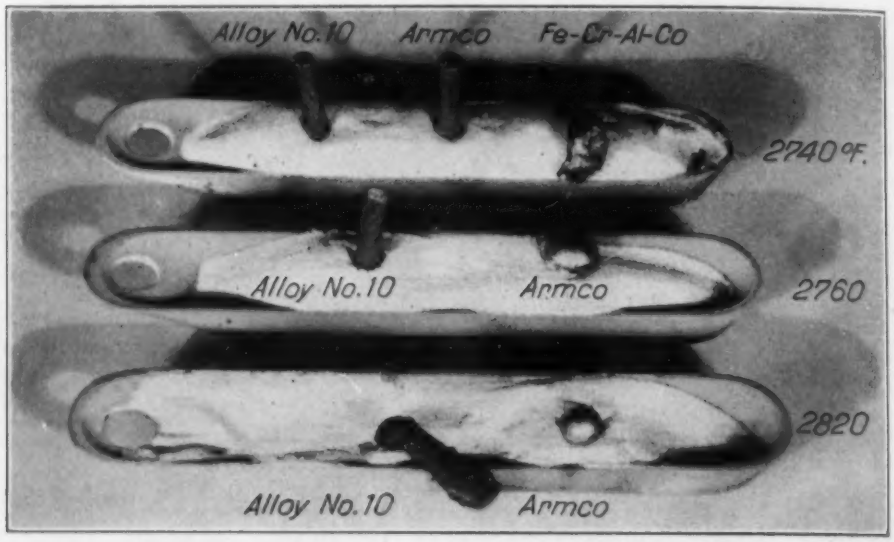


Fig. C—Showing the Results of Melting Point Tests.

really adequate data at present on creep. For the greater part, however, these matters relate to the actual utilization of this material in furnace operation and inasmuch as we are not expert along this line we shall have to refer to those who must necessarily take up these things in a practical way.

Mr. Knapp asks questions relating to growth and life. At this time I cannot add anything to the discussions already made on these points. Instead I would refer Mr. Knapp to the manufacturers of electric furnaces who use Alloy No. 10.

Coming to the comments of Mr. Koch we naturally appreciate them very much. Mr. Koch has had much to do with the development of the application and use of this alloy. As a matter of fact, for a long time we have looked to the Hevi Duty Electric Co. for guidance and support in carrying the experimental work on this alloy to its logical conclusion. By this I mean the use of the material in actual furnaces. This is not the first time I have been engaged in developing a new product which shows sufficient promise to justify expectations for a very definite and healthy commercial use of it, and I would like to give my testimony as a technical man to the value of what I might call "stout backing" during the development period. Mr. Smalley and Mr. Koch of the Hevi Duty Electric Co. provided the stout backing for this development.

Mr. Waldrip has submitted an interesting discussion on the Fe-Cr-Al-Co alloy KANTHAL which should be useful at this time when new high tem-

perature heating elements are being seriously considered. At the outset Mr. Waldrip states that our paper, and particularly the discussion, tends to show poor results for the Fe-Cr-Al-Co alloy. If that has been the impression gained from our presentation, we are happy to have the opportunity to correct it. What we did show was an accurate comparison between the Fe-Cr-Al-Co alloy and our No. 10 alloy at temperatures which appear to us to be suited to reliable comparisons. We would not draw the conclusion suggested by Mr. Waldrip that our tests show a "marked increase in resistance throughout the useful life" or a "comparatively short life at high temperatures" for the Fe-Cr-Al-Co alloy. We believe our test data indicate a long useful life at temperatures well above those obtainable with the nickel-chromium alloy. As for the melting point, our slide shows what we observed on the melting points. We realize that certain determinations made in Europe have shown some variability in the melting points of these or similar alloys. The results of some careful determinations of the temperature of incipient fusion were reported in the paper while in the discussion we gave visual evidence of the relative fusion temperatures of these alloys and pure iron. With the samples inside a hydrogen furnace and under constant observation with the optical pyrometer, we do not see how there can be any gross errors in our determinations or how there can be any error in the relative fusion points.

Mr. Waldrip also suggests that we show excessive growth and low mechanical strength at high temperatures for the Fe-Cr-Al-Co alloy. Actually all we did was to show what difference we found for growth between it and the No. 10 alloy, though we included no data on strength. In general, Mr. Waldrip's comments leave us with the impression that he feels our discussion tended to show that the one alloy was suited by its properties and behavior to high temperature operation, and that the other was not. We made no such statement and do not intend to make such an application. Mr. Waldrip's own comments on the successful use of the Fe-Cr-Al-Co alloy KANTHAL are good evidence that such is not the case.

Mr. Waldrip comments on the difference between the results of the accelerated life tests and furnace performance. The life test is useful for determining relative high temperature stability but the conditions are so severe that one can expect a better performance in a furnace, unless other factors enter which alter the normal behavior. In this light the life test results reported in the paper and in the discussion, for all alloys covered, should be interpreted as giving relative high temperature stability in air. The normal element life in a furnace under proper application conditions will be much greater than the life in the test. This is an important point and has been covered in the paper. Incidently, while our standard life test temperatue is 2600 degrees Fahr. (BBT), the comparison referred to by Mr. Waldrip was made at 2500 degrees Fahr. (BBT), see Fig. B.

Mr. Waldrip comments on previous alloys of Fe-Cr-Al which have been made in Europe. These were mentioned in the paper, and they originated in the early Marsh alloy of 1913, insofar as our information goes. We feel that it has been not alone the cold brittleness of such alloys which has impeded their introduction, but rather the metallurgical difficulties and actual hazards which are met in the production of aluminum alloys. While several methods

can be used to make such alloys, we felt strongly that a new melting practice would be required for safe operation and to give reproduceable and reliable results in order to secure control of the condition of the alloy, its chemical composition in major and minor constituents, and physical properties. We regret that we cannot discuss this matter in detail at this time for we believe it is pertinent in connection with the point raised.

The comments on cold ductility do not require special mention for we have covered that point in our paper and there seems to be nothing to add.

Finally Mr. Waldrip notes that we do not discuss applications of Alloy No. 10. At A. O. Smith we have had furnaces under observation but we have had relatively little to do with that end of this development and hence we made no effort to cover the field.

THE AGING OF STEEL

By E. S. Davenport and E. C. Bain

Abstract

The paper deals first with the moderate increase in hardness which develops gradually in annealed low carbon steel at temperatures as low as room temperature following a rapid cooling from temperatures near 1300 degrees Fahr. (700 degrees Cent.). This is explained on the basis of precipitation of iron carbide from ferrite supersaturated with respect to carbon, a reaction which conforms in type with those in familiar age-hardening alloys.

More extended studies are reported on the aging phenomena observed at temperatures from zero centigrade upward in cold-worked low carbon steel. Observations from many sources are considered, which, as summarized, indicate that strain-aging, "blue brittleness," the Fry etching figures and other behaviors are all due to the precipitation, particularly upon slip-bands, of a compound, probably an oxide, from ferrite supersaturated with respect to oxygen. This precipitation reaction shows some seemingly unique features.

I. General Introduction

THE term "aging" as applied to steel has covered a wide variety of slow, gradual changes in properties which are characterized by taking place, apparently spontaneously, after the final intentional treatment. Possibly undue significance has been attached to the appearance of spontaneity merely because the changes occur at ordinary natural temperature, say between 100 and —20 degrees Fahr. (40 and —30 degrees Cent.), at which temperature most materials give one the impression of being quite permanent and unchanging. But there is really nothing specially significant, so far as the metals are concerned, about "ordinary" or "room" temperature; nothing which should argue for the absolute inertness of metal maintained in this range. Indeed, in some metals, notably lead and tin, full

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. Of the authors, E. S. Davenport is associated with the Research Laboratory of the U. S. Steel Corp., Kearny, N. J.; and E. C. Bain is assistant to vice president, U. S. Steel Corp., New York City. Manuscript received June 1, 1935.

annealing may occur at these temperatures. While the reactions which occur in steel at such low temperatures are very greatly retarded as compared with the more obvious, or even spectacular, reactions which occur in short time intervals at, for example, a red heat, there is, nevertheless, sufficient activity possible at room temperature to alter the properties of steel and other metals profoundly. The apparent general stability of metals at ordinary temperatures and the rareness of any very serious aging effects have been rather misleading as regards the actual prevalence of low temperature phenomena.

While some of the early reports of such aging behavior are not very concise and therefore difficult of verification, there is no longer any doubt whatsoever of definite changes in properties in various steels occurring while the metal is merely remaining at ordinary temperatures. The changes in properties merely proceed at rather slow rates and fortunately, in many steels, the changes are not of a character to be of serious import for engineering purposes.

Recently the term aging has been more specifically applied to only a few of the most familiar phenomena, the nature of which is rather better understood. The manner of the change in properties, as it varies with the composition of the steel, or with the actual temperature of the metal during aging, is curiously similar in a large number of examples of slow, spontaneous change; and this pattern, which is followed so generally, serves not only to characterize and group together the aging processes, but also to suggest the type of fundamental reaction responsible for the aging.

In this discussion some of the well recognized changes in properties designated as aging will be described in sufficient detail to warrant an enquiry into a possible mechanism of aging which would explain the observations. One definite viewpoint will be maintained throughout, chosen because of its usefulness in the interpretation of the involved data; it may be stated briefly as follows:

Aging is a process in which the trend is *toward* a restoration of real equilibrium, constitutional or mechanical, and *away from* an unstable condition set up by a previous final operation, e.g., cooling abruptly from other temperature ranges or a mechanical treatment introducing stresses. The approach to equilibrium in a system which has, by one means or another, been forced into an unstable state is always a time-consuming process—the actual time ranging from fractions of a second to years or even, so far as one can estimate, an infinite period, depending upon conditions. The reactions involved

in the aging of steel proceed at a fairly wide range of velocities, depending upon temperature and the particular types under consideration, but, fortunately, they proceed at such velocities as permit the property changes to be conveniently observed in minutes, hours, or days and are therefore, in general, splendidly adapted to laboratory study without special equipment on the one hand, and without too great delay on the other.

In some examples of aging the precise identity of the elements responsible for the property change has not as yet been determined while in other cases there seems to be no ambiguity in the data and the precise reaction can be identified. Generally, however, one can now narrow the probable responsibility for the aging to one or more of two or three possibilities. It is significant that manufacturers may now produce steel at will, by special methods suggested by systematic study, which are free from certain undesirable types of aging.

As examples of gradual changes of properties in iron and steel one might call to mind a number of such phenomena:

The gradual apparent toughening, after rolling, of medium and high carbon steel such as rails.

The increase in hardness of freshly-quenched tool steel in the period of perhaps a week after hardening (as very accurately reported by Sykes).

The loss in coercive force, accompanied by increased maximum induction, in permanent magnet steels following hardening.

The change in magnetic properties of silicon transformer sheet; indeed essentially all aging phenomena appear, for some reason, to involve changes in magnetic properties.

However, the present discussion relates to the commercially important changes which occur in soft steel either as a consequence of rapid cooling or of cold work. There are three principal manifestations of such slow alterations of properties:—

A. To one of the three most important examples of aging, found in practically all soft steels, the designation "carbon aging" has been given for the purposes of this discussion. It has also been called "sub-critical quench-aging." It is most frequently observed in annealed wire and sheet which may have possessed a low hardness value and high ductility immediately after annealing, but which, after a few weeks storage, is found to have become harder and to have lost some of its ductility. In the subsequent detailed account of

this type of aging the role of carbon will be discussed and the reason for its designation will become apparent. It should be stressed that this type of aging is restricted to annealed metal free from cold work which has been cooled rather rapidly in the range below 1100 degrees Fahr. (600 degrees Cent.).

B. In all respects the most complicated example of aging is that of "strain-aging," a type of spontaneous property change which results after, and seemingly requires, cold deformation as the significant conditioning operation. An idea of its complexity may be inferred from the fact that the basic causes of strain-aging seem likewise to be responsible for "blue brittleness" and even to some extent for caustic embrittlement, not to mention the extraordinary hardness developed in steel while being rolled or drawn in the temperature range around 400 degrees Fahr. (200 degrees Cent.). It may be said that the very profuseness of the data on this phenomenon has been responsible for the delay in its clarification; the observations on the phenomenon have been made at such a wide variety of temperatures that the tests and the conditioning treatments were hopelessly confused. Had all the actual testing been conducted at a single temperature level at which aging was sufficiently slow as to be negligible, much of the complexity might never have appeared.

C. The term aging has been applied to a most extraordinary change in plastic properties which low carbon steel undergoes while in the process of strain-aging. Indeed, to some metallurgists, this behavior rather than those described under B has come to connote aging after straining; the most, however, that can accurately be stated at present is that the two effects appear to run concurrently.

Ordinary low carbon steel, e.g., of the rimming type, when annealed exhibits a peculiarity when undergoing deformation which has not been definitely observed in nonferrous metals. If a strip of such steel is stressed in tension up to the limit of elasticity, it abruptly yields and elongates, in one or two places, very considerably. The abrupt yield may locally reduce the section of the test piece by as much as ten per cent. In a tensile testing machine the sudden marked elongation may suffice to reduce the load as much as fifteen per cent below that which the steel prior to yield was able to carry without any permanent deformation. The conclusion must be drawn that any portion of the metal which has been deformed a little by slip-plane movement is weaker than the undistorted crystals—a condition apparently unique for iron. When the elongation in the de-

formed regions has progressed to a certain degree, these regions, in spite of the diminished cross section, resume normal metal behavior and become stronger, even, than the full, unreduced section of the specimen, whereupon new regions yield suddenly. This intermittent yielding generally continues until there is no undeformed metal left in the gage section, although the specimen may break before all the metal yields. The steel specimen then elongates precisely as does a nonferrous metal.

This curious property of iron may be illustrated in another very simple way. Let a short, slightly curved piece of copper or brass wire be held with thumb and finger pressing against the ends. When the thumb and finger are brought nearer together the wire bends more or less uniformly to a shorter radius of curvature. If now an annealed soft iron wire be held similarly and likewise bent by approximating thumb and finger, the first bend will be very sharp and entirely local. The sudden yield is quite perceptibly noted as a loss of resistance to the pressure. Perfectly cylindrical tubes can be loosely rolled from brass sheet but the same equipment may produce merely a many-sided prism of soft iron. Tin-plate cans occasionally exhibit this phenomenon.

Deep drawing or stamping brings out this yield phenomenon very clearly and the zones of sudden marked elongation are called "stretcher strains" and for some applications constitute a serious shortcoming in annealed soft steel. But the remedy is simple. Any sort of cold deformation, even slight, which positively causes a small but definite slip in each grain clearly puts the metal into the second condition of the tensile test and the sudden local yield and the resulting stretcher strains disappear. This is accomplished by a stretcher leveling, a pinch pass, or roller leveling, the last mentioned having peculiar advantages. No appreciable hardening, in the ordinary sense, accompanies this method of preventing stretcher strains, nor is there detectable change in thickness of the sheet, for the sheet is merely bent back and forth by passing staggered rolls under definite pressure.

At this point the element of aging enters. The effect of any of these light cold-working treatments to destroy the marked yield point soon wears off in the case of ordinary low carbon steel or wrought iron. A few weeks at room temperature or a few minutes at, for example, 400 degrees Fahr. (200 degrees Cent.) suffices to restore the metal to the condition permitting stretcher strains. The lightly

worked metal, if stored too long before forming or stamping, must then be retreated by cold work to restore the desired condition.

Now the recovery of the marked yield point, after its effacement by cold work, occurs at a rate which fairly well parallels the strain-aging of the same steel and may probably have some relation to that phenomenon, but as yet this is somewhat problematical.. At any rate, steels have been made which, once lightly cold-worked, do not regain the stretcher-strain condition even in some 18 months, but it must be stated, such steels are not entirely free from strain-aging. Such steels have been designated "non-aging" steel, and there is certainly no valid reason why this gradual change from the non-yielding to the marked-yielding condition after cold work should not be classed as aging. The value of a steel which retains indefinitely its acquired freedom from stretcher strains is not necessarily very great, for roller leveling or a similar operation can usually be performed on steel just prior to forming, and at a cost which is in no sense prohibitive. In some particular instances the retention of the desired condition may constitute a fairly valuable improvement. The non-aging steel, like all annealed iron yet produced, is prone to stretcher strain, except as given some sort of cold work; the difference lies in the *rate* of change from the cold-worked state, which is almost negligible in non-aging steel.

In the studies to be reported, the gravest difficulty was that of the over-lapping of two (or more, perhaps) types of aging in the same investigation. All results therefore must be most critically examined for this confusing shortcoming. It is believed that the interpretations offered are free from this criticism.

Selection of a Criterion of Aging

Although some examples have been mentioned wherein aging is seemingly manifested by a mere dissipation of internal stress, the preponderance of evidence points to one general cause of aging phenomena. The following pages will show that aging is unquestionably caused, in the general case, by definite changes in the constitution of the metal; more particularly, it is the formation of a compound and its precipitation out of the solid solution in the form of minute particles, which is responsible for the changes incurred during aging. Since this has been well established, (and nothing will be found in the present report to cast any doubt on this explanation) it

would appear preferable to select as a criterion of aging the estimation of some property which depends as closely as possible upon particle precipitation. The following tabulation indicates the broad scope of some of the many phenomena which accompany aging and which therefore might be the subject of investigations into aging:

Crystallography by X-ray Diffraction
Magnetic Properties
    Coercive Force
    Remanence
    Maximum Inductance
    Permeability at Constant Field-strength
Electrical Conductivity (or Resistivity)
Density or Dimensional Measurements
Rate or Mode of Corrosion
Mechanical Properties
    Tensile Strength, Yield Point, Elastic Limit, Reduction of Area, Elongation, Impact Resistance (Energy of Breaking), Hardness (Brinell, Rockwell, etc.).

The magnitude of change in a few of the features mentioned above is too slight to constitute a useful measure of aging. Of the others, the basis for rejection is somewhat as follows:

Coercive force (magnetic) appears to depend largely, perhaps almost wholly, upon internal stress which, while undoubtedly a variant with aging, is yet not directly a measure of its progress. Different alloys change during aging in a quite different manner as indicated by coercive force and no broad correlation seems possible. Great care must be exercised in handling specimens to avoid introducing stress externally.

Electrical conductivity measurements require extremely precise technique (in spite of some reports) when small changes are to be recognized. Ambiguities have already been noted.

Density changes are a secondary effect and not immediately interpretable. The preparation of specimens suitable for precise study is expensive, and the actual determination is extremely time-consuming.

X-ray diffraction study is admirably suited to broad investigations upon aging, but not particularly well suited to the attack employed in this inquiry.

Corrosion behavior has been used successfully as a rough criterion of the presence or absence of aging but is not susceptible of refined evaluation. An extended discussion of a typical application

of this method will be found below under the discussion of strain-aging.

Mechanical properties are the most promising but ordinary tensile specimens, in the large numbers required, are costly to prepare. In cases wherein the tensile test has been employed the yield point has proven a good criterion, difficult though it is of evaluation.

Impact strength is usually measured in terms of energy (foot-pounds or KgM) absorbed in breaking a beam specimen of standardized dimensions by a heavy pendulum. Although it is a more conveniently applied test to break a specimen, (usually notched opposite the point of impact) by a pendulum whose potential energy is known, the energy absorbed is, generally speaking, precisely the same as though the force were applied more gradually and the figure for energy (or more accurately, work) then computed from the area under the recorded stress-strain diagram. The figures from this test may, in some cases, be greatly changed by aging of the specimen, but in other cases they are not much affected, as shown by Jungbluth in 1930 (Kruppsche Monatshefte, Vol. 11, p. 117 "Werkstoffe für Dampfkesselbau"). Some tests made in the present study indicated that without special care and restrictions the method is not suited to a broad investigation of the mechanism of aging, although in specific instances the test is of direct value in studying the relative merit of steels. A further word may be of interest at this point.

If, for any reason, rupture occurs in an impact specimen substantially without any plastic deformation (shear) then the energy absorption is inevitably very small with attendant lack of accuracy in its estimation. A standard Charpy specimen of a fairly strong material under these conditions absorbs only some 0.3 foot-pounds. As the same specimen begins to exhibit some plasticity the value for foot-pounds absorbed increases very rapidly until the specimen finally does not break at all but instead merely bends in the Charpy machine. In this latter range all precision is again lost. As a result, impact tests show a supersensitivity over a narrow range of properties and unsatisfactorily uniform results outside the range. Advantage has been taken, however, of this very circumstance to illustrate in a most spectacular way the effect of aging upon impact properties. Temperature of test, next to the character of notch, is the most effective factor in determining energy absorption. With a notch of carefully chosen depth and sharpness, specimens of any steel can be made to fail in the brittle manner (low impact) at low

temperature and in the plastic manner (high impact) at slightly higher temperature. The change may be fairly abrupt with respect to temperature as shown by Strauss and Fry in 1921 (Kruppsche Monatshefte Vol. 2, p. 126; "Rissbildung in Kesselblechen"). It has been shown by Jungbluth, in the paper referred to above, that aging shifts the temperature range of rapid change in impact value toward higher temperature. In the case of a non-aging material exposure of specimens to aging treatments results in no shift of the supersensitive range of testing temperature, while susceptible materials during aging lose impact strength in all temperature ranges and therefore appear to have a shift in the critical impact temperature range. (See Fig. 20.)

This very emphatic demonstration demands a number of specimens to cover the temperature range of testing and requires very high precision in notching for comparing one steel with another, and yields no direct quantitative measure of the progress of aging. Care must be taken to suit the notch to the material so that the temperature of rapid change will be below the temperature of moderately rapid aging—otherwise testing and conditioning will be confused.

Accordingly, this method, although valuable and convincing for certain comparisons was rejected for the present study. Of the various properties proposed as criteria for aging, both logic and expediency lead to the choice of penetration hardness. The actual number set down from this physical measurement is, regrettably, highly empirical, but the fundamental physical property responsible for the measurement is well defined. Particle precipitation is, first of all, without exception accompanied by a resistance to plastic flow, or more fundamentally, an increase in elastic limit in shear, for deformation in metals occurs by slip along crystal planes. Aging may or may not restrict the maximum degree of such slip, the *capacity* for deformation, but it invariably increases the resistance against it. Penetration hardness testing is properly applied only to materials, such as steel, which develop no actual ruptures in the test, and accordingly the penetrator under a definite load continues to advance into the metal until the resistance to plastic flow (shear) just balances the force on the penetrator. The conical, spherical, or pyramidal penetrator during loading presents an ever increasing area to the metal under test, and hence a lower and lower specific stress is impressed upon the metal up to the moment of its arrest. Its penetration depth is definite and constitutes primarily an evaluation of the shear resist-

ance of the metal, with some dependence, however, upon the *increase* in shear resistance caused by the deformation resulting from the test itself. A small, easily prepared specimen suffices for following the change in room temperature hardness of a material during aging, and this circumstance permits many more determinations for the same outlay of time and effort than would be possible if any of the other suggested criteria of aging were employed. Throughout this report many charts are shown which portray the change in hardness and other properties with lapse of time; except in two instances, Figs. 14 and 20, the property tests were all made at room temperature, 70 degrees Fahr. (20 degrees Cent.).

The development of an increase in hardness by any means in any of the ordinary steel compositions is accompanied by a loss in elongation and reduction of area in the tensile test. The hardness increase during aging likewise follows this general rule and one correlation of these changes will be shown to illustrate the close parallel (Fig. 10).

The torsion test is an excellent primary criterion of aging and an example of its use will later be shown under the discussion of strain-aging.

II. Quench Aging or Carbon Aging

The type of aging observed in annealed, low carbon steel containing about 0.04 to 0.12 per cent carbon is believed to be an example of the familiar precipitation hardening of alloys of which, perhaps, duralumin is one of the more widely known. This principle elucidated by Merica and Waltenberg is now so well known as to make extended discussion unnecessary. A solid solution supersaturated by rapid cooling from some high temperature subsequently develops, at some lower temperature, a shower of particles of the solute metal, or compounds thereof, in the release of this supersaturation. This precipitation or age-hardening temperature may be as high as 1100 degrees Fahr. (600 degrees Cent.) or below room temperature, depending upon the alloy. Only a few general features need be mentioned here:

For any age-hardening system the higher the aging temperature employed the shorter the time of reaching maximum hardness.

The lower the temperature of age-hardening maintained for this optimum period, the greater the degree of hardening.

Maintaining the aging temperature beyond this optimum period

causes reduced hardness and it is possible first to harden and then to soften the metal at a given temperature. This so-called "over-aging" involves coalescence of the precipitated particles.

Little hardening and more loss in ductility occurs when the rejected phase forms primarily in grain boundaries. Such alloys will age harden when cold-worked to produce loci of precipitation generally throughout the body of the grains.

When the compound formed during aging is composed of very unlike elements, hardening is likely to occur at relatively low aging temperature and very much higher temperatures are necessary to permit softening by over aging.

One general aspect of age-hardening systems should perhaps be mentioned. It is convenient to speak of the hardening as caused by fine particles, and one frequently hears the phrase "critical particle size" as meaning that magnitude of the individual particle exerting the maximum hardening effect—as though some smaller (or larger) particle has an inferior hardening power. This simple picture has never been verified; the observed hardening effect may really result scarcely at all from those particles which are recognizable in any way or which cause the cloudy darkening of the prepared microscopic sample, but rather from the entirely invisible action of pre-precipitation phenomena. In certain alloys this is almost positively the case and one may perhaps more safely attribute most age-hardening of precipitation alloys to the first disturbance of the solid solution prior to the formation of any discrete particles however small. Certainly there is no reason to think that there is any uniformity of particle size. However, this is a point of only minor importance here and is brought out only to explain the later discussions of aging in steel wherein it will be stated that the attempt to observe precipitated particles under the microscope is not very successful.

The type of constitution in a binary alloy system requisite to possible age-hardening is shown in Fig. 1, and the progress of hardening with increasing aging period at various temperatures in the familiar iron-tungsten alloy is shown in Fig. 2. (Data compiled in part from work of Sykes.) Some of the features mentioned above are well illustrated in this chart.

Carbon Solubility in Alpha Iron

For simplicity it has been customary to speak of carbon as be-

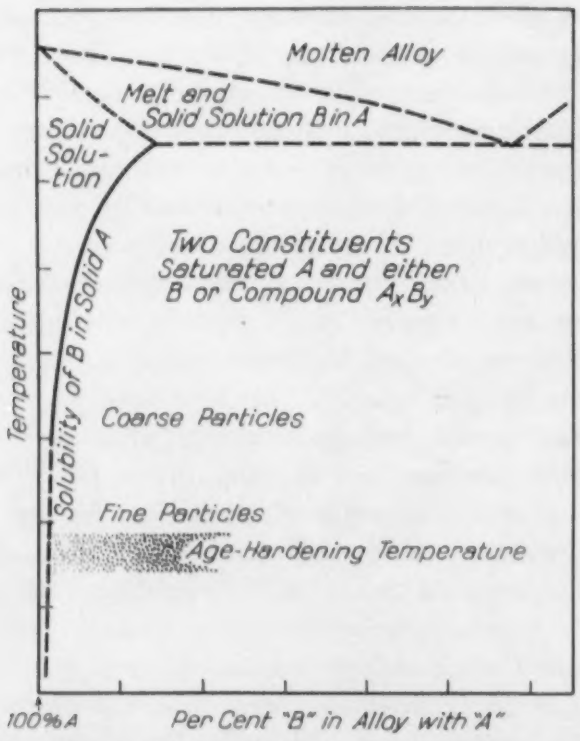


Fig. 1—Typical Constitution Diagram Illustrating the Solid Solubility Characteristics Necessary for Age Hardening.

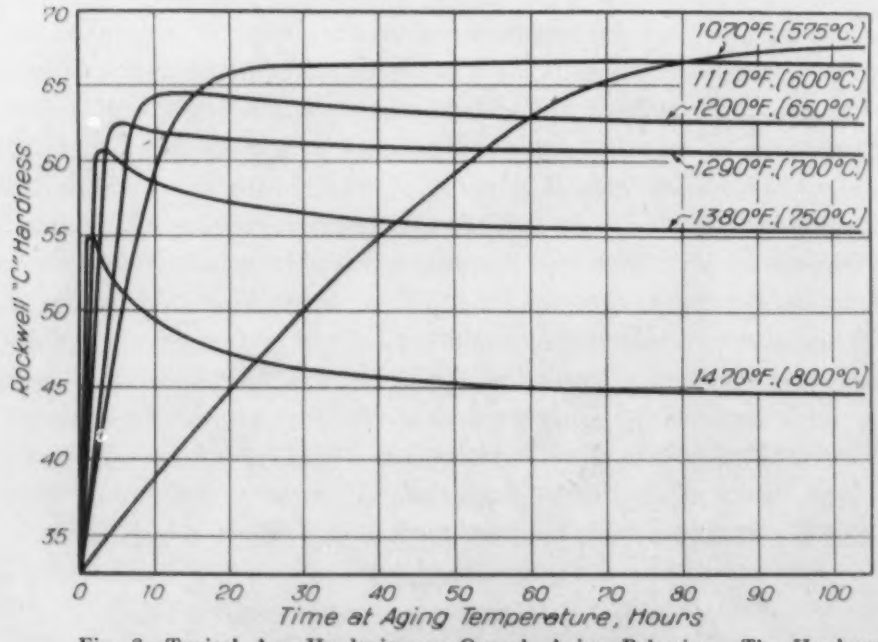


Fig. 2—Typical Age Hardening or Quench Aging Behavior. The Hardness of a Quenched 75 Per Cent Iron—25 Per Cent Tungsten Alloy After Aging at the Various Indicated Temperatures (Sykes).

ing insoluble in the low temperature, or alpha, allotropic form of iron and moderately soluble in the high-temperature, or gamma, modification. The whole art of heat treating tool steel depends in a sense upon this abrupt change in solubility of carbon. Actually, carbon is not insoluble in the low temperature form of iron, although the carbon solubility does suddenly decrease some 15-fold as the iron transforms from the gamma form (austenite) to the alpha form (ferrite). In all ordinary steels, the undissolved

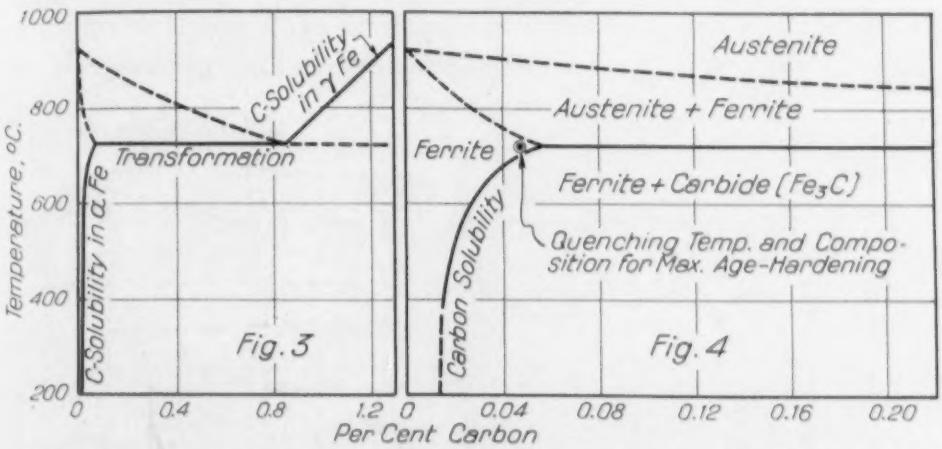


Fig. 3—Portion of Iron-Carbon Constitution Diagram Showing Solubility of Carbon in Alpha- and Gamma-Iron.

Fig. 4—Portion of Iron-Carbon Constitution Diagram With Carbon Scale Extended to Emphasize the Solubility of Carbon in Alpha Iron and the Age Hardening Potentialities of the System.

carbon contained in the iron-carbon alloy is in the form of iron carbide, or cementite (Fe_3C), and in discussing the solubility of carbon it is assumed that some of the carbide is present. Pure iron, in the absence of carbon, transforms only at about 1675 degrees Fahr. (910 degrees Cent.) but with sufficient carbon present, the transformation occurs at about 1345 degrees Fahr. (730 degrees Cent.). The solubility of carbon in iron is shown in Fig. 3 and the contrast between alpha and gamma iron is well marked with respect to capacity for dissolving carbon. The present interest centers in the relatively low solubility of carbon in alpha iron at temperatures below about 1345 degrees Fahr. (730 degrees Cent.).

In Fig. 4, the same solubility curve of Fig. 3 is drawn with a much extended abscissa (carbon content) so that the change of solubility of carbon in ordinary iron below 1345 degrees Fahr. (730 degrees Cent.) is more apparent. By comparison of Fig. 4 with Fig. 1, it will be seen that iron-carbon alloys with only a few hun-

dredths per cent carbon, and even when heated not above 1300 degrees Fahr. (700 degrees Cent.), possess the requisites for potential age-hardening. That ordinary low carbon alloys are in reality mildly age-hardening will be shown by the observations which follow.

Age-hardening of Quenched Low Carbon Alloys

In spite of the high solubility of carbon in iron (gamma) at temperatures above the critical temperature 1345 degrees Fahr. (730 degrees Cent.) the effective maximum of carbon is dissolved in ferrite (alpha iron) at this temperature for in low carbon steels the

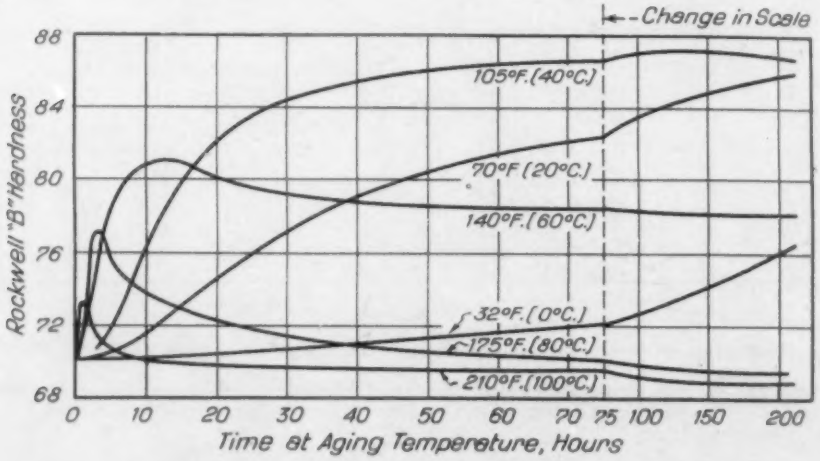


Fig. 5—Quench Aging of 0.06 Per Cent Carbon Steel, No. 1. Hardness After Quenching from 1325 Degrees Fahr. (720 Degrees Cent.) and Aging at the Various Indicated Temperatures; Plotted on Linear Time Scale.

extra carbon dissolved in gamma iron is rejected on even fairly rapid cooling at the halt in cooling occasioned by the evolution of heat in the steel during the allotropic transformation. In any event, in the case of steels carrying less than about 0.055 per cent the whole of the carbon is dissolved at about this temperature. The following account of the age-hardening of low carbon steels relates to a quench from 1325 degrees Fahr. (720 degrees Cent.) in all cases except as otherwise designated.

In Fig. 5 is shown the hardness increase in a steel of 0.06 per cent carbon during aging at the indicated temperatures 0, 20, 40, 60, 80, and 100 degrees Cent. (32, 70, 105, 140, 175, and 210 degrees Fahr.) after quenching from 720 degrees Cent. (1325 degrees Fahr.). It will be noted that the age-hardening proceeds more and

more rapidly with increase in reheating or aging temperature, but that the maximum hardness achieved is less in the case of the higher temperatures. This chart is characteristic of the familiar age-hardening alloys; the similarity in the behavior pattern to that of Fig. 2 is far too close to be fortuitous.

The suspicion has already pointed to carbon solution and subsequent dispersed precipitation as an almost inevitable cause of some age-hardening in steel and the aging behavior shown in Fig. 5 is found in essentially all low carbon steels, but the case is not thereby

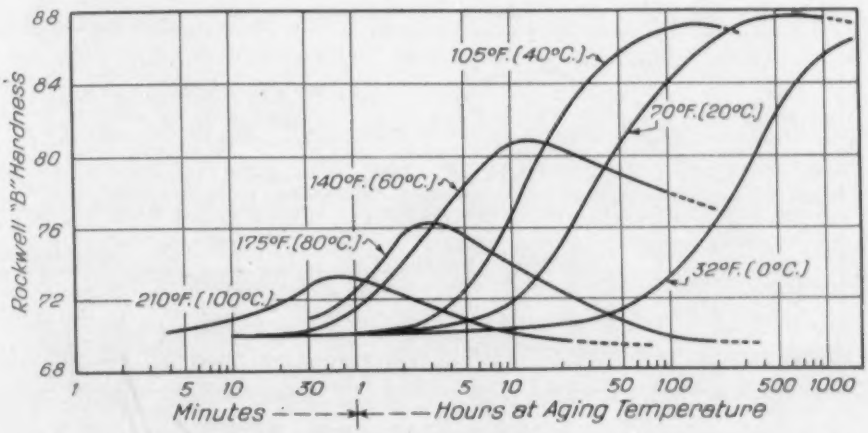


Fig. 6—Quench Aging of 0.06 Per Cent Carbon Steel, No. 1. Extended Data of Fig. 5 Plotted on Logarithmic Time Scale.

unequivocally proven for carbon, for some other element may have been passing in and out of solution during the treatments applied with the intent of bringing about carbon reactions. The evidence pointing toward carbon as responsible for quench-aging appears in subsequent paragraphs.

It is highly desirable to show, on one chart, the slow hardening of the metal at low temperatures and also the rapid, though less intense, hardening at elevated temperatures. The disparity in rates, however, is so great that a single chart of the ordinary sort would reveal no detail whatsoever of the behavior of the material at the higher temperature. Accordingly, a logarithmic scale for time (abscissa) has been used frequently in this report. The same data plotted in these two ways appear in Figs. 5 and 6. The unfamiliarity of the logarithmic plot is of no great disadvantage, since the actual time intervals are shown, and, in any event, one soon grows accustomed to its peculiarities.

In connection with the general discussion of age-hardening alloy systems, it has been pointed out that reheating in some temperature ranges first hardens and then softens the metal. Thus in Fig. 5 or Fig. 6, the hardness of the low carbon steel may be seen to reach a maximum and then to diminish when aged at temperatures above 105 degrees Fahr. (40 degrees Cent.). Within 200 hours the hardness of specimens re-heated at 175 degrees Fahr. (80 degrees Cent.) is reduced essentially to the original hardness. Higher aging temperatures cause the steel to pass through the hardening cycle and to

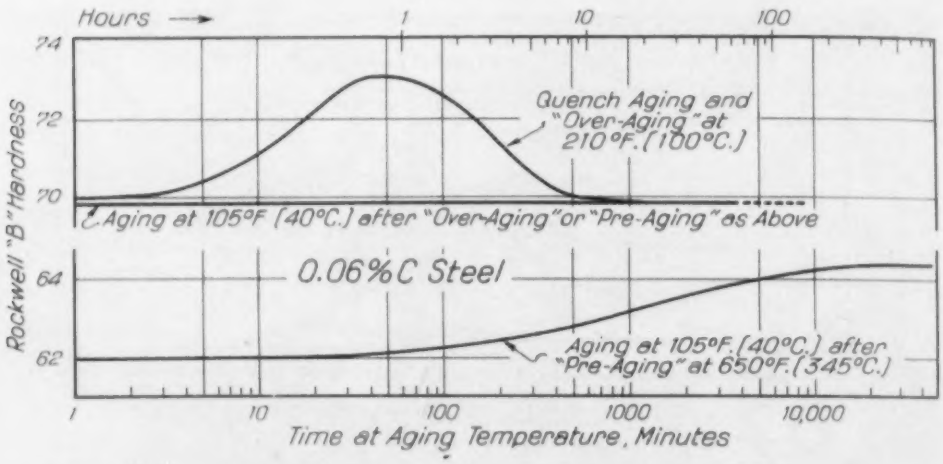


Fig. 7—Upper Block—Quench Aging and "Over Aging" of Steel No. 1 at 210 Degrees Fahr. (100 Degrees Cent.) Followed by Aging at 105 Degrees Fahr. (40 Degrees Cent.); Note Absence of Age Hardening at 105 Degrees Fahr. When Such Aging is Preceded by the "Over Aging" Treatment.

Lower Block—Quench Aging of Steel No. 1 After "Over Aging" at 650 Degrees Fahr. (345 Degrees Cent.); Note Small but Definite Amount of Age Hardening Due to "Over Aging" Temperature Being Too High.

regain softness with even greater rapidity. This circumstance of final softening after some precipitation hardening is due to the coalescence of the carbide particles to form individual fragments of carbide too large to be effective as a hardening agent. At the same time, apparently all the carbon in excess of the solubility limit for the aging temperature involved is rejected. The resulting structure, in which relatively large carbide particles are distributed in an iron matrix whose content of dissolved carbon is now very low, may even be softer than the freshly quenched structure to which the dissolved carbon contributes some hardness.

If an aging treatment has resulted in the rejection of essentially all the dissolved carbon and, at the same time, has sufficed to produce a dispersion of no marked hardening power, then the metal is in a

permanent state which will not change substantially thereafter. Such metal will be spoken of as "over-aged" or as "pre-aged," although it might well be designated as "equilibrated." This is a very important means of stabilization and can usually be applied to any alloy system wherein an insoluble phase separates out of a supersaturated solid solution. The effectiveness of the treatment may be seen in the upper portion of Fig. 7 in which the hardness of the specimen first pre-aged at 212 degrees Fahr. (100 degrees Cent.) is shown as reheated at 105 degrees Fahr. (40 degrees Cent.). No detectable hardening results at 105 degrees Fahr. (40 degrees Cent.) in the specimen already pre-aged rapidly at a somewhat higher temperature. The course of the pre-aging at the higher temperature is also shown in Fig. 7.

If the pre-aging be performed at considerably higher temperature, the carbon solubility may be sufficient at this temperature to leave a significant amount still in solution. In this case, a heating at a much lower temperature results in some age-hardening. The effect of attempting to pre-age at too high a temperature is illustrated in the lower portion of Fig. 7, wherein the aging treatment at 105 degrees Fahr. (40 degrees Cent.) following a pre-aging at 650 degrees Fahr. (345 degrees Cent.) is shown to cause a definite, though relatively small, hardening effect. It should be noted that such a pre-aging is merely equivalent to the use of a rather low quenching temperature.

These examples provide a basis for some generalizations concerning stabilization and metallurgical equilibria in general. Whenever it is desired to forestall slow, gradual changes toward equilibrium in alloys which by virtue of previous heatings are out of equilibrium at the service temperature, they may be more or less stabilized by a heating at a temperature slightly above the service temperature. The following principles then apply:

1. The time interval of heating for pre-aging should be as long as possible, limited only by practical or commercial expediency.

2. The temperature selected should then be the very minimum which in the time interval available just contrives to bring about a substantial completion of the reaction, so far as that temperature is concerned. This condition may be recognized by the extremely low rate of reaction, or of property change, during the final part of the heating interval.

3. Once determined, this time-temperature combination repre-

sents the pre-aging treatment of maximum effectiveness. More than its results are not possible.

4. The degree of effectiveness of such a treatment depends upon the temperature interval between pre-aging temperature and the service temperature. When this is relatively great, the condition resulting from the pre-aging treatment may be sufficiently different from that which would ultimately result at the service temperature as to allow of some further changes.

Usually a very effective pre-aging treatment can be devised when the service temperature is relatively low. The only usual difference in equilibrium properties between service temperature and that chosen for practical pre-aging is in the solubility of some phase, which solubility in iron changes rather slowly with temperature in the low ranges. We shall, however, have occasion to refer to an example presently wherein it is difficult to devise a satisfactory pre-aging treatment.

It has been observed by other investigators that the actual numerical hardness change during carbon aging is slight in the higher carbon alloys carrying 0.10 to 0.15 per cent carbon, and that the age-hardening is practically absent in 0.20 per cent or higher carbon material. There is reason to believe that the increase in hardness is actually most pronounced in material carrying not more than 0.04 per cent carbon which is not sufficient, even, to fully saturate the ferrite at the quenching temperature. By way of explanation, it must be recognized that the usual hardness scales, particularly the Rockwell scale, are purely arbitrary and that their sensitivity varies from range to range. This circumstance makes a precise study of this curious effect of carbon content difficult. One may say, however, that the low carbon iron is so rapidly hardened by the increase of *permanent* carbide as pearlite, or interstitial or spheroidized cementite, that it is not surprising that a small change in the hardness of the soft iron phase would less and less affect the aggregate hardness as more and more residual carbide is present. At any rate, during the present study, the more emphatic hardening in the low carbon ranges, 0.03 to 0.05 per cent has been confirmed as well as the very slight response to aging of the 0.15 to 0.20 per cent carbon material. No particular significance is thought to attach to this circumstance.

Carbon Primarily Responsible for Quench Aging

The most direct experimental approach to the question of the

responsibility of carbon for quench aging is by the examination of iron substantially free from carbon; with pure iron, carbon-free iron containing significant amounts of other extra-analytical elements may be compared.

Electrolytic iron, for example, is generally very low in carbon, but it carries as much oxygen as many of the low carbon, soft commercial steels, indeed often more oxygen than carbon. Such mate-

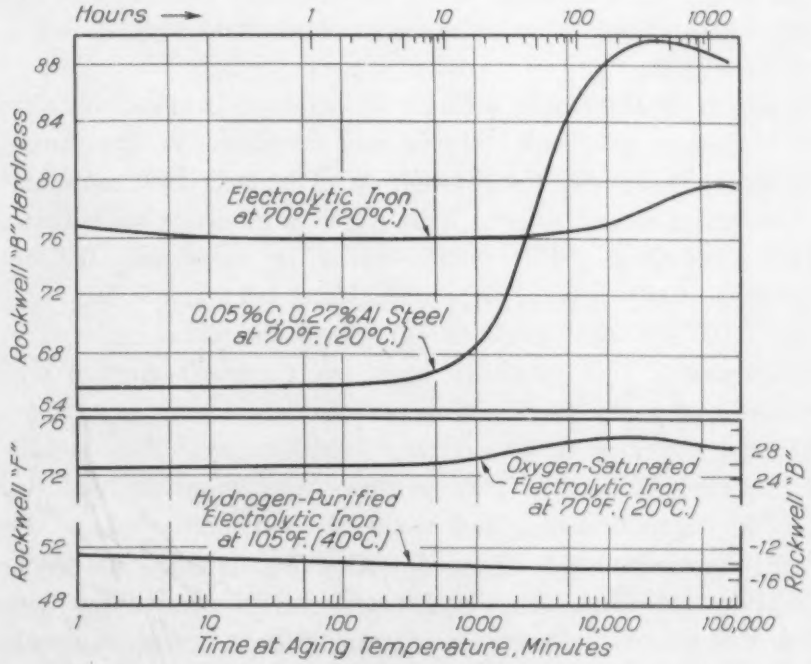


Fig. 8—Upper Block—Quench Aging of Electrolytic Iron, No. 2, and of 0.27 Per Cent Al Steel, No. 3, at 70 Degrees Fahr. (20 Degrees Cent.); Note Wide Disparity in Degree of Age Hardening.

Lower Block—Quench Aging of O_2-Saturated Electrolytic Iron No. 4, at 70 Degrees Fahr. (20 Degrees Cent.) and H_2-Purified Electrolytic Iron at 105 Degrees Fahr. (40 degrees Cent.); Note Absence of Significant Age Hardening.

rial, available for this study, carried about 0.02 per cent carbon and about 0.022 per cent oxygen. Its response to aging after quenching from about 1325 degrees Fahr. (720 degrees Cent.) is practically nil, as shown in the upper portion of Fig. 8. This failure of very low carbon iron, carrying a relatively large amount of oxygen, to exhibit age-hardening not only strengthens the belief that carbon is the element involved in quench aging, but also strongly suggests that oxygen, under these conditions, does not dissolve and re-precipitate as a fine general dispersion of iron oxide to cause significant hardening.

To verify this inference still further, some of the electrolytic iron was melted, maintained at high temperature under high vacuum and then finally severely oxidized with pure iron oxide under only moderately reduced pressure. Such material is undoubtedly free from carbon and nitrogen, but saturated with respect to oxygen. This material, however, likewise failed to age harden significantly after quenching, as may be seen in the lower portion of Fig. 8. Very pure iron, as might be expected, when purified for considerable time in hydrogen also failed to exhibit age-hardening, as also shown at the bottom of Fig. 8.

While it is extremely difficult to produce iron-carbon alloys in which oxygen is practically absent and in which, at the same time, the carbon is uniformly distributed, nevertheless, the examination of such a material would offer a final item of evidence with respect to the role of carbon. For this purpose, a substitute for such a homogeneous oxygen-free carbon steel has been employed. It consists of 0.05 per cent carbon, soft steel carrying some 0.27 per cent aluminum. The solubility of oxygen even in molten steel, in the presence of a few hundredths per cent aluminum is so low as to preclude the evolution of CO during solidification. The solubility of oxygen in the presence of 0.27 per cent aluminum at 1325 degrees Fahr. (720 degrees Cent.) then must be vanishingly small. Hence, in effect, one is dealing with an oxygen-free material in the case of the 0.27 per cent aluminum alloy, insofar as the ferrite is concerned.

Yet this material shows very strong quench-aging properties, as may be seen in the upper portion of Fig. 8. It should be mentioned that while the aluminum alloy may contain nitrogen, the proportion of aluminum present and the heating for quenching are such as to practically necessitate the permanent fixing of the nitrogen so that the aging temperature could have no effect upon the condition of the nitrogen. One is forced to conclude from these various observations that carbon alone, by dissolving and re-precipitating, can cause the phenomena of age-hardening after quenching. While it seems probable that only carbon alone is involved in the age-hardening after subcritical quenching, one cannot as positively state that nitrogen plays no part in the aging as ordinarily observed.

The case for nitrogen as being responsible for quench aging appears very weak for a number of reasons. In the first place, in spite of a marked disparity with respect to nitrogen content in open-hearth and Bessemer steel, the two types of material age after quench-

ing very similarly as may be seen in Fig. 9. The aging temperature involved is 70 degrees Fahr. (20 degrees Cent.). The actual content of nitrogen, moreover, found in most of the materials tested is below the solubility generally assigned to this element even at low temperatures. If this be correct, then any aging caused by nitride precipitation must occur under conditions definitely different from those of the present quench aging study. There is at least some rea-

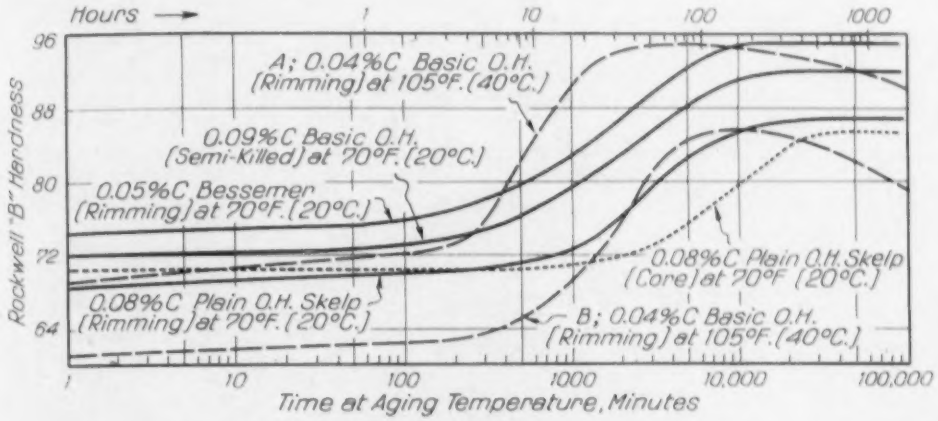


Fig. 9—Quench Aging of Various Steels: No. 5 Bessemer; No. 6 Semi-Killed Basic O. H.; No. 7 Plain O. H. Skelp (Rim and Core); All Aged at 70 Degrees Fahr. (20 Degrees Cent.); Also Two Rimming Basic O. H. Steels, No. 8 (A) and No. 9 (B) Aged at 105 Degrees Fahr. (40 Degees Cent.).

son to believe that much higher concentration is necessary in the case of nitrogen in order that supersaturation and subsequent precipitation may occur than in the case of either carbon or oxygen; furthermore, combination and precipitation can occur only at distinctly higher temperature and nitrogen diffuses at a slower rate than carbon.

The Quench Aging of Various Steels

In Fig. 9 are grouped the aging curves of a number of materials which have been investigated in the course of these studies. They are representative of the behavior of a larger number of miscellaneous materials which have been studied in the laboratory. For comparison purposes the rim and core zones of a rimming steel were studied separately and the aging behavior of each is set forth in Fig. 9. Similar steels of Bessemer and open-hearth origin are likewise contrasted. In Table I the compositions of this group are set forth along with the analyses of the special materials referred to earlier.

A number of almost universal trends have been correlated in

Table I
Analysis of Materials

Steel No.	C	Mn	Si	P	S	Al	O_2	N_2	Description
1	0.06	0.40	0.009	0.012	0.031	.....	0.020	0.0042	Basic O.H. rimming steel
2	0.020	.....	.....	.....	.....	.....	0.022	0.0007	Electrolytic iron
3	0.05	0.09	0.01	0.005	0.033	0.27	0.002	0.0092	Aluminum-bearing steel
4	0.007	0.003	0.005	0.013	0.008	0.002	0.045	0.0043	Oxygen-saturated electrolytic iron
5	0.05	0.34	0.008	0.096	0.055	.....	0.027	0.011	Bessemer steel (rim)
6	0.09	0.39	0.029	0.016	0.057	.....	0.025	0.004	Basic O.H. semi-killed steel
7	0.08	0.47	.....	0.008	0.027	.....	.....	.....	Plain O.H. skelp
8	0.04	0.16	.....	0.012	0.032	.....	0.025	0.0034	A.—Basic O.H. rimming steel
9	0.04	0.12	.....	0.012	0.030	.....	0.035	0.0033	B.—Basic O.H. rimming steel
10	0.05	0.14	.....	0.010	0.027	.....	0.031	0.0016	C.—Basic O.H. rimming steel
11	0.14	0.49	0.05	0.012	0.020	.....	0.005	0.0052	Commercial non-aging steel

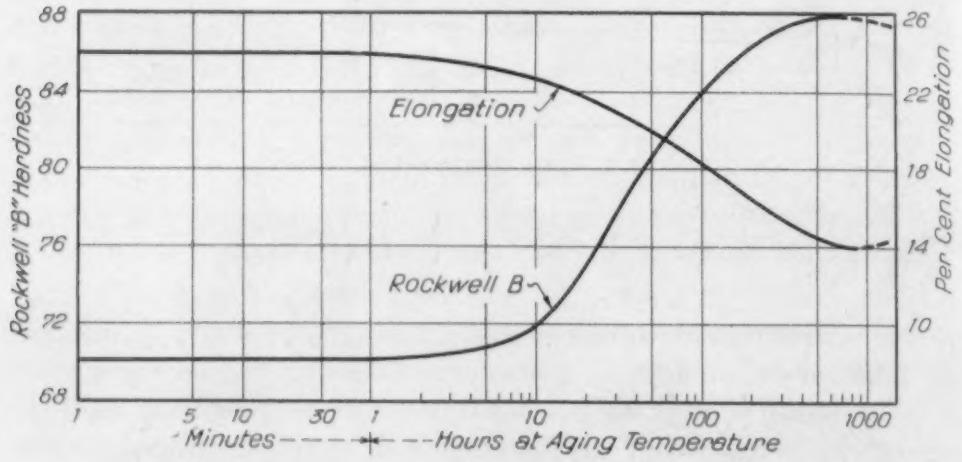


Fig. 10—Quench Aging of a Low Carbon Steel at 70 Degrees Fahr. (20 Degrees Cent.) as Measured by Both Rockwell B Hardness and Per Cent Elongation in Tension.

steels of the same type as influenced by any single variable; thus the so-called plastic features in the tensile test, elongation and reduction of area, invariably decrease with increase of yield strength and hardness. This same close concurrence is found also in aging steels. This is well illustrated in Fig. 10 in which the elongation is found to be gradually changed at about the same rate as is the hardness of a low carbon steel during aging.

III. Strain-Aging

The type of aging now referred to most often is that occurring in steel which has been subjected to some cold deformation, e.g., cold-

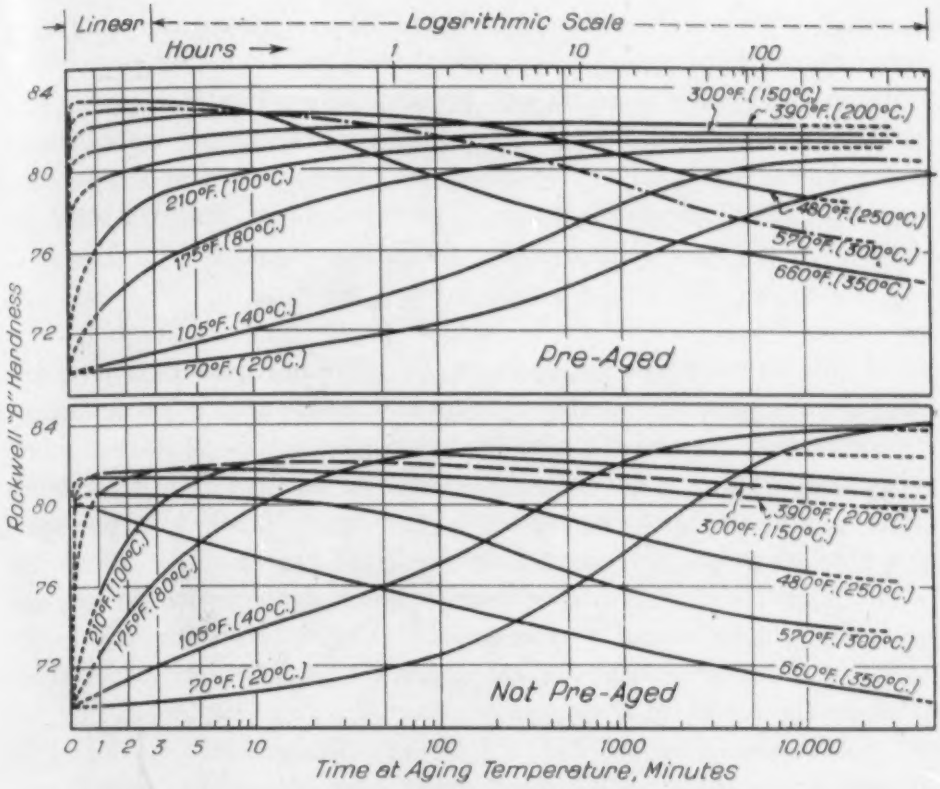


Fig. 11—Upper Block—Strain Aging of Steel No. 8; Hardness After Cold Rolling Followed by Aging at the Various Indicated Temperatures; All Pre-Aged Before Cold Rolling.

Lower Block—Strain Aging of Steel No. 8 Employing Same Technique as Shown in Upper Block Except That Pre-Aging Before Cold Rolling Was Omitted.

rolling or wire drawing, and is designated "strain-aging." The metal is, of course, somewhat hardened at once by the cold work but instead of acquiring only this usual and familiar increase in hardness, it is observed that most low carbon steels continue to harden for some time after the cold working operation. During the ensuing weeks in storage, the steel continues to harden at a diminishing rate and to lose, at the same time, some of its apparent ductility. Following even a relatively small amount of cold work, such as represented by a five per cent reduction, for example, almost all low carbon steels undergo this type of aging. A degree of cold work corresponding to ten or fifteen per cent reduction of cross section appears to result in the most intense changes during aging; this is approximately the deformation provided as the conditioning treatment in the examples illustrated here.

As in quench aging of low carbon steel and all other varieties

of aging observed, the rate at which the changes occur increases with the temperature of aging. Although there is no reason, *a priori*, why two types of reaction could not proceed at very similar rates, the specific time-temperature relationships are, in general, highly characteristic for each variety of aging and the most enlightening approach to an aging problem, then, is through its time-temperature pattern.

The Peculiarities of Strain-Aging

Fig. 11 shows how the room-temperature hardness of a low carbon steel changes, (following a uniformly severe cold deformation as a conditioning treatment) after increasing intervals at a variety of aging temperatures. In order to isolate the particular type of aging under study, the material shown in the upper block was pre-aged in a manner to put the metal in a stabilized condition as far as the reactions involved with any ordinary quench-aging in this range are concerned. The actual pre-treatment prior to cold work was 17 hours at 212 degrees Fahr. (100 degrees Cent.) which successfully stabilizes the metal by aging and over-aging. (See Fig. 7).

An examination of Fig. 11 reveals immediately a distinctly unique pattern of aging behavior, apart, even, from the necessity of cold work as a conditioning treatment. The outstanding characteristics of this strain-aging which may lead to a closer acquaintance with its causes are as follows:

1. The maximum hardness is not so definitely the result of the low temperature and long time combination already discussed under quench-aging; on the contrary within wide limits the higher the aging temperature, the greater appears the hardening.

2. Softening by over-aging does not occur in just the same manner as it does in quench-aging systems. As shown in the case of carbon aging, this softening is observed after treatment at temperatures only a little above those which will cause moderately rapid hardening. Instead, in strain-aging, a most unusually wide range of temperatures will cause practically maximum hardening without subsequent softening even in a time interval of 500 or 1000 hours.

3. Hardening is outstandingly rapid even at temperatures so low as to give no indication, in a very long time interval, of final softening.

These characteristics suggest a certain type of precipitation reaction which may be regarded as extreme, reflecting simultaneously (1)

a very high formation activity and (2) a very low diffusion rate.

For convenient comparison, Fig. 11 shows the pure strain-aging effect (upper block) upon hardness in contrast to the combined effect of strain-aging and carbon-aging upon hardness (lower block). The most interesting feature of the comparison is the relative unimportance of the additional carbon, or quench-aging insofar as the magnitude of the hardening is concerned. As a means of reducing the total effect of aging in cold-worked material the pre-aging treatment described above is of no very great value. Nevertheless a behavior of fundamental importance is shown in the un-pre-aged specimens (lower block). The hardness in this case reaches a higher maximum in the long time and low temperature treatments than in the short time and higher temperature combinations, a behavior characterizing the usual age-hardening systems—iron-tungsten, duralumin, etc.—and a feature of carbon aging. The comparison therefore serves to corroborate the inference that this strain-aging is the result of a rather unique combination of factors in iron alloys.

The Nature of Strain-Aging Reactions

By the simple expedient of pre-aging, the effect of the cold work as the principal conditioning treatment may be isolated, and it is reflected in the strain-aging hardness curves of Fig. 11. By means of this pre-treatment one may then be assured that if particle precipitation is responsible for the hardening the system must be of the sort, already described, which requires the disordered condition of slip planes in the grains or grain boundaries for precipitation. Grain boundary precipitation alone, unlike general particle precipitation, causes very little hardening. Chromium carbide precipitation in annealed austenitic stainless steel is an excellent example of the type in which the compound rejected from solid solution confines its location to the grain boundaries in annealed material but is precipitated in a thoroughly general manner in grains which are traversed by slip bands. In the latter case the hardness is strongly affected by particle rejection. The demonstration of the purely grain boundary rejection of the compound responsible for strain-aging in low carbon steel will be described subsequently.

The particular behavior of strain-aging as set forth in Fig. 11 would appear to be explained most satisfactorily by certain plausible assumptions.

1. In forming the precipitate the iron probably combines with a very different element, in the chemical sense, for the tendency toward combination appears relatively strong, occurring, as it does, at low temperature in spite of low diffusivity. This inference is not *necessarily* correct but carries, at least, a high degree of probability.

2. The tendency for diffusion of the other element involved must be very low—unlike carbon—otherwise coalescence resulting in softening would promptly follow hardening.

3. The increase, with aging temperature, in the extent of zones within the metal wherein precipitation is possible is a natural consequence of the cold work preceding precipitation. Portions of the grains are still, even after very great deformation, of sufficiently perfect crystallinity as to be substantially free from precipitation. Intermediate between these undistorted crystal blocks and the slip planes of maximum disturbance are regions of slight disorder in which precipitation may occur at the higher but not at the lower temperatures. Accordingly, the seemingly anomalous behavior of low temperatures being incapable of producing an ultimate hardness as great as some higher aging temperature is explained. It is significant that such behavior has not been found in age-hardening alloys free from cold work.

In brief, strain-aging is a unique, or at least rare, type of aging which, however, is explainable on the basis of particle precipitation by assigning certain reasonable, if unusual, habits to the precipitating compound. The compound forms from the iron and the other element in supersaturated solid solution (1) at rather low temperature, but (2) only at interfaces (grain boundaries or slip bands). The particles do not grow to ineffectually large size at the expected temperatures because (3) of low diffusion rate and perhaps unusual stability of the first crystallites, both of which may, indeed, be reflections of the same fundamental property.

Mode and Rate of Corrosive Attack

Many examples have been found wherein the precipitation of particles from supersaturated solid solution brought about by an intermediate reheating is accompanied by a tremendous change in corrosive attack. Indeed, at the moment the authors are inclined to suspect that this is perhaps superficially the most outstanding single characteristic of particle precipitation. By way of actual demonstra-

tion one may quench (and roll for strain-aging) the whole or a short bar of the solid solution alloy and then reheat the bar at temperatures increasing from one end to the other. It is convenient to place one end of the quenched bar in cold water and apply the torch to the opposite end. A reasonably uniform and regular thermal gradient is soon established between the desired limits, and may be maintained as long as necessary. If now one of the long faces of the bar is used for observation a complete series of constant time and variable temperature reheatings is encompassed in the one specimen. When the long face is exposed to suitable corrosive agents it will be found that a certain zone of the bar will be preferentially attacked, and apparently without exception, a black band may be developed across the specimen corresponding to a certain average size of particle precipitated within a certain temperature range.

This has been accomplished for a number of alloys:

Alloy	Compound
Al-Cu	$CuAl_2$
Fe-Cr	$FeCr$
Fe-W	Fe_2W_2
Fe-Co-W	CoW (Fe_2W_2)
Fe-Mo	Fe_2Mo_2
18-8 Stainless Steel	Cr_4C
High Speed Steel	Fe_4W_2C — Fe_2W_2 (?)
Quenched Tool Steel	Fe_3C
Quenched Low Carbon Steel	Fe_3C
Strained Low Carbon Steel	FeO (?)

It will be noted that the last item of the series listed is the case under consideration. Some ingenuity has been exerted in discovering a suitable etching agent for the corrosive attack in many cases, and to Fry belongs the credit for developing a very satisfactory agent for darkening the precipitation zone in strain-aged mild steel. Quite clearly, when the actual volume of the precipitated compound is small the contrast in appearance between the aged and un-aged metal is likely to be slight. In general, it appears that the precipitated particles are themselves not much attacked and remain upon the metal as a dark "powder" while in general their presence accelerates the corrosive action. The intensity of the etching effect rarely, if ever, corresponds to the intensity of the age-hardening. The darkest etching zone almost always is found in the particular metal heated to a rather higher temperature, or for a much longer period than that which results in the maximum hardness. This is true in the case of the Fry reagent on strain-aged material. However, since crystallites

must first have been very small before they can have grown, by coalescence, to larger size, the dark etching corrosion behavior is therefore a reliable test for the presence of age-hardening, although not a dependable measure of its degree.

Fry has found that bars of mild steel when deformed by bending acquire the capacity for dark etching after being heated into the range of rapid aging. Very interesting patterns are developed in steel only slightly deformed, and then reheated. The only regions

Fig. 12—Development of Stretcher Strains in Flat Tensile Specimen of Low Carbon Steel.
A. Stretcher Strains (Upper Portion of Photo) After Initial Loading to Just Above Yield Point; Unetched.
B. Same as A After Aging 30 Minutes at 480 Degrees Fahr. (250 Degrees Cent.) and Etching in Fry's Reagent.
C. Same as B After Second Loading to Just Above Yield Point (Opposite Side of Specimen); Elongation in Second Loading Took Place in Bottom Portion of Specimen as Shown.
D. Same as C After Polishing Transversely with Fine Emery Paper; Note How the Prior Deformed and Aged Zone Stands Out in Relief.

blackened by the reagent are those in which the deformation brings about general precipitation, and these zones mark certain regions of high shearing stress. These appear to be the same as the Lüders lines observed long ago. Most annealed steel shows the unique property of yielding suddenly and very considerably in certain separate stressed regions instead of generally in all regions in proportion to the stress. This circumstance gives rise both to the Lüders lines and the figures developed by the Fry reagent. The black etched bands constitute an almost conclusive proof that precipitation is responsible for strain-aging.

The manner in which the Fry reagent may be employed to em-

phasize, on the etched metal surface, the subtle differences between aged and un-aged low carbon steel is shown in a simple experiment. Photographs at half natural size in Fig. 12 illustrate the various steps of the experiment. A tensile specimen, preferably of a soft steel subject to stretcher strains, is loaded until a fair elongation occurs at one end of the gage section. With wide specimens the metal yields in a more picturesque pattern but even the one-inch section illustrated here shows a broad zone of elongated metal with a narrower branch. In this instance the specimen elongated purely elastically with no permanent deformation until a load of 1050 pounds was applied, whereupon sudden marked yielding took place and the load dropped to 850 pounds. Thereafter the load fluctuated erratically between 850 and 920 pounds as new blocks of material yielded with the roughened zone spreading as a wave slowly down the specimen. The metal which yields first is distinguishable both by its reduction of section and a peculiar roughened or matte surface texture. View A is typical of stretcher straining in a flat tensile bar. If the specimen is now immediately etched in the Fry reagent there is no detectable difference between the attack in the deformed and in the undeformed zone, and no added contrast is developed. However, if one now ages the specimen at some 400-500 degrees Fahr. (200-250 degrees Cent.) then the etched surface of the specimen reveals a marked difference between undeformed and deformed zones, because presumably only the deformed zone contains the fine precipitate. View B is of the same specimen as A after aging and etching. The darkly etched zones are about 10 per cent thinner than the light zones, and the photographs give some suggestion of the very definite reduction of cross section by the relief effect. In any event, as has been shown, the aging treatment (one half hour at 250 degrees Cent.) must have hardened the material very definitely in the deformed zone, and if so its elastic limit in tension must have increased. The proof of this may now be seen by replacing the specimen in the tensile test machine and reloading. The behavior, as before, is purely elastic until a load of 1050 pounds is applied, whereupon yield begins in the undeformed region (not in the reduced section) and the load thereafter varies erratically between 850 and 920 pounds as the zone of deformed metal widens and sweeps slowly over the specimen. The previously reduced and aged section is not further reduced and continues to resist deformation, by virtue of its greater strength, until the cross section in the unaged region is now very

greatly reduced as in View C (opposite side of specimen from Views A and B). The darkly etched metal is now in relief with the unaged material in intaglio. Further to establish this point, the face of the specimen has been abraded transversely with emery paper and is shown in View D. The difference in width between the major portion of the prior deformed zone and the latter unaged deformed zone is itself a convincing proof of the marked strengthening by the aging, which, however, is conditioned by cold work.

It is interesting to consider another aspect of the corrosive action of etching agents on aged material. Marked hardening of deformed metal by aging occurs in a few days or weeks even at room

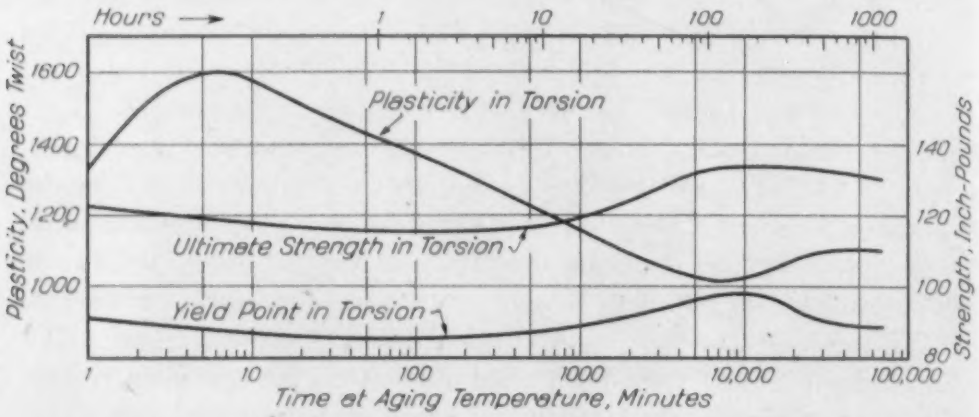


Fig. 13—Strain Aging of Steel No. 8 As Measured by Torsion Test. Cold-Rolled, Aged at 105 Degrees Fahr. (40 Degrees Cent.) and Tested at Room Temperature.

temperature but only when the aging is carried out at temperatures above 250-300 degrees Fahr. (120-150 degrees Cent.) does the surface etch differently from unaged material. Even six months aging at room temperature which produces very marked hardening exerts no effect on etching characteristics. One must therefore assume that the fine precipitate which seems necessary for black etching is not necessary at all for hardening; this point cannot be over-emphasized since some theories ignore this fundamental observation.

Other Evidences of Strain-Aging

1. Special Mechanical Properties—While penetration hardness is an excellent measurement with which to correlate the process of aging, any type of physical test which reflects the resistance to shear may be relied upon to provide an indicator of the course of aging.

Thus the torque required to produce the first permanent twist in a torsion test (yield-point in shear) may be used as a means of following precipitation hardening. Since precipitation hardening is usually (though not invariably) accompanied by a loss of plasticity the same test often provides another criterion of aging in the form of the angular displacement through which the applied torque may twist the specimen prior to rupture. The maximum recorded torque is also indicative of the progress of aging. These observations are plotted, in Fig. 13, against interval of aging time at 105 degrees Fahr. (40 degrees Cent.) for a series of specimens of low carbon steel of the rimming type. In this case wire of steel No. 8 was conditioned by a cold reduction of about 12 per cent and then tested at room temperature after various intervals at 105 degrees Fahr. (40 degrees Cent.). It will be seen that with aging the resistance to shear increases while the plasticity diminishes.

2. *Blue Brittleness*—Even the older text books and other treatises on soft steel point out that in the temperature range above about 300 degrees Fahr. (150 degrees Cent.) cold work produces a much greater hardening effect than the same degree of deformation on the same soft steel at ordinary room temperature. Furthermore, the reports often mention that nearly, if not quite, the same extra hardening results if the metal after working at room temperature is then heated into a similar temperature range. This second observation has already been adequately discussed in the preceding pages on strain-aging. At any rate, the peculiar, inordinate hardening found in rolled or drawn soft steel when the metal in process reaches a temperature of about 400 degrees Fahr. was called "blue brittleness," because it was thought that the most effective temperature was such as to cause a surface oxidation or "temper color" of just the right characteristics to appear blue by the thin film effect. However, when precise study was begun, it became apparent that different investigators of simultaneous heating and working, using different means of cold work, were securing accurate results in which the temperature of maximum effectiveness differed. As it happens this discrepancy affords a valuable clue to the mechanism of blue brittleness.

In general, the investigators who employed annealed steel and the impact test found a high temperature necessary for the maximum hardening and loss of ductility while those utilizing the tensile test reported a lower temperature as being the most effective. The impact test, of course, is an extremely rapid application of stress and

causes deformation in a very brief time while the specimen at controlled elevated temperature in the tensile machine is in the state of deformation for a vastly longer time. In short, the two tests suggest that merely unusually rapid strain-aging may explain the phenomenon. A lower temperature with longer time in the tensile machine is substantially equivalent to the shorter time at higher temperature in the impact test. Some further consideration, however, is necessary.

It has been commented upon already how very rapid is the acquisition of hardness in strain-aging at any temperature above some 200 degrees Fahr. (100 degrees Cent.) even though strain-aging is deliberate enough at room temperature. Indeed, in order to get any notion of the rate at which hardness is developed at the higher temperatures very small samples, already cold-worked, had to be plunged into molten lead-bismuth alloy for the aging treatment of a few seconds and then into water—otherwise, at these higher temperatures the maximum hardness was reached (and often passed) before the metal could be cooled and tested for room temperature hardness. This method was employed to secure the short time data of Fig. 11.

The hardening in strain-aging is the result of two factors (1) deformation to form slip bands and (2) a suitable time interval at aging temperature. The interval may be exceedingly short (fractions of a second) if the temperature is relatively high—400 degrees Fahr. (200 degrees Cent.), for example. While, in general, the two necessary conditions are actually realized by first putting the metal into the cold-worked state and then providing the short interval at elevated temperature this precise sequence of events is not the only one capable of developing hardening by strain-aging. It is equally effective to heat the annealed metal and then to apply the cold work at the elevated temperature whereupon the metal begins instantly to age harden at the rate corresponding to the temperature. A great many of the earlier studies were thus made upon annealed material at temperatures of rapid age-hardening in which the cold-working requirement was supplied by the test method itself. Thus a specimen of annealed low carbon steel may be heated to some 150 to 250 degrees Fahr. (65 to 120 degrees Cent.) in a suitable accessory oven and the cold work then applied, for example, by the tensile testing machine to which the oven encasing the specimen is attached. Upon each slip plane, as it is formed, precipitation, and its accompanying hardening, begins at once and a marked hardening effect thus follows closely upon the deformation, lagging perhaps only by a fraction of a second

at most. By the time the specimen is loaded to the breaking point almost the whole of the deformed specimen is in the age-hardened condition and its breaking strength as measured is very considerably increased over that found in an identical specimen tested at room temperature, at which age-hardening requires several days to be noticeable. In the case of such investigations the testing was in reality a part of the conditioning treatment; the metal, if restored to room temperature before final breaking, still possesses the high strength and low ductility.

Turning to the impact test wherein again annealed metal is heated to successively higher temperatures for breaking, a certain temperature is discovered at which, if the notch is properly acute and deep, the metal shows a low energy absorption. In this case aging must be well nigh instantaneous to effect the impact behavior for, clearly, aging after the specimen is broken will have no effect. Accordingly, the temperature of maximum effect upon impact tests is higher and the effect is less marked than in the tensile test. Nevertheless, there is evidence that aging is able to keep pace, to some extent, with the cold work and thereby influence the behavior of the specimen even under this test. It should be noted that even intergranular precipitation may aid in producing a brittle type of impact fracture and hence a low energy of breaking. Similar temperature regions of anomalous high hardness have been found using the Brinell hardness test, lying intermediate between those found by the impact and the tensile test.

The most striking example of working in the "blue" range is that of rolling under conditions wherein the heat of deformation raises the temperature into the rapid aging range. In successive passes, particularly, the metal becomes very hard and the reduction in thickness is accomplished only by considerably increased roll pressure. If the metal is kept below the aging temperature, lower roll pressure suffices to effect even greater deformation, provided of course, that the temperature is not so extraordinarily low as to bring in the naturally greater hardness of any metal at very low temperature. The rapid hardening of soft steel by working at the strain-aging temperature is likewise observed in wire drawing and useful advantage is taken when higher strength is desired in the product. Coils, either of wire or strip, lose heat relatively slowly and the very maximum aging may easily result if the heat of deformation raises the metal temperature considerably. The exact temperatures involved

may be approximately estimated from the curves of Fig. 11 by assuming a suitable rough estimate of the period over which the coil remains in the rapid-aging temperature range.

A very interesting and illuminating experiment by Körber serves to elucidate the behavior of metal which undergoes deformation, and therefore becomes amenable to strain-aging, in a temperature range

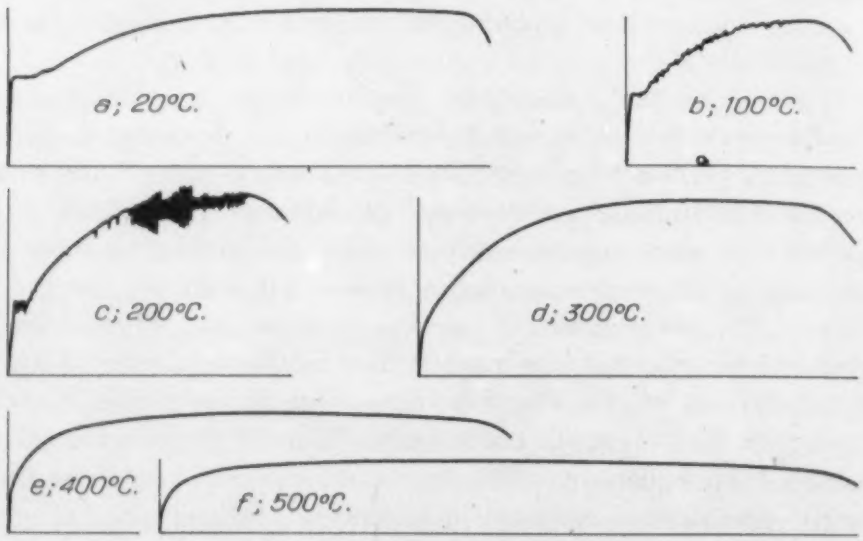


Fig. 14—Stress-strain Curves Obtained on Low Carbon Steel at Various Elevated Temperatures Showing Marked Oscillations in the Curve C Obtained at 400 Degrees Fahr. (200 Degrees Cent.) (Körber).

which causes very rapid age-hardening. This experiment is really only a tensile test at 400 degrees Fahr. (200 degrees Cent.)—one of a series at various temperatures. The stress-strain diagram C in Fig. 14 shows an oscillating load which is only barely suggested in the curve of the test at 212 degrees Fahr. (100 degrees Cent.) and absent in the curves for other temperatures.

The oscillation of the load-recording mechanism implies some slight periodic irregularity in the elongation of the specimen since the actual movement of oil in the hydraulic loading system is inherently smooth and uniform. The high amplitude of the oscillations suggests that some approximate reasonance was established between these irregularities and the natural frequency of the oscillating part of the testing machine. In all probability the frequency of the oscillation was actually determined by the pendulum of Körber's testing machine. However, the important point is that at 400 degrees Fahr. (200 degrees Cent.) the rate of strain-aging is beginning to be very

rapid indeed, and that only in this temperature range do the oscillations reach high amplitude.

It is believed that there is a definite relation between the rate of strain-aging and this extraordinary stress-strain diagram, curve C; the mechanism appears to be somewhat as follows:

1. Some of the metal elongates abruptly causing a drop in load and a falling of the pendulum.

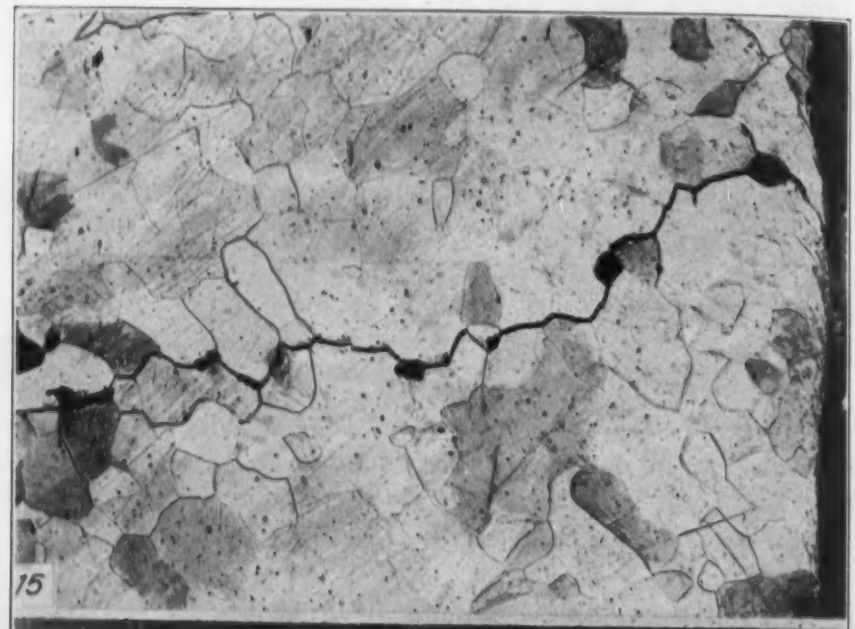
2. For a brief period the load is so reduced that no further elongation occurs, but during this brief interval the deformed, and hence conditioned, metal ages quickly and acquires a high elastic limit.

3. By the time the load is again built up, partly, of course, by the falling pendulum itself, the slightly deformed metal is too greatly strengthened by aging to elongate, and the full elastic limit of the neighboring section must be exceeded again. During this cycle the pendulum has made its complete to-and-fro motion.

4. If the aging rate is such as to accomplish substantial strengthening during the pendulum's half cycle then the oscillation may reach a very considerable amplitude; nor need the synchronism be very precise to accomplish the oscillation.

Clearly this process can go on best in that part of the test in which a large portion of the metal has already been strained to induce some strain-aging. At any rate the oscillations are of such a frequency as to fit in well with both the probable natural frequency of the pendulum and the estimated rate of age-hardening. At 570 degrees Fahr. (300 degrees Cent.), curve D, the aging rate is so rapid as to require no perceptible period for the strengthening action and accordingly no oscillations can be set up. While some irregularities would certainly be found in other types of testing machines it is nevertheless believed that the pendulum contributes very largely to the high amplitude of the effect.

3. Intergranular Precipitation and Corrosion Embrittlement—The view that strain-aging is brought about through the precipitation of an iron compound which, however, does not form generally throughout the perfect crystal grains of annealed material, is strengthened by evidence of another sort. It has been seen how the slip bands traversing the worked grains constitute loci for precipitation and by analogy, there is every reason to suspect that in annealed, or only slightly worked metal, the grain boundaries would likewise constitute suitable locations for compound rejection. This situation might be expected to reveal itself either by a loss of intergranular



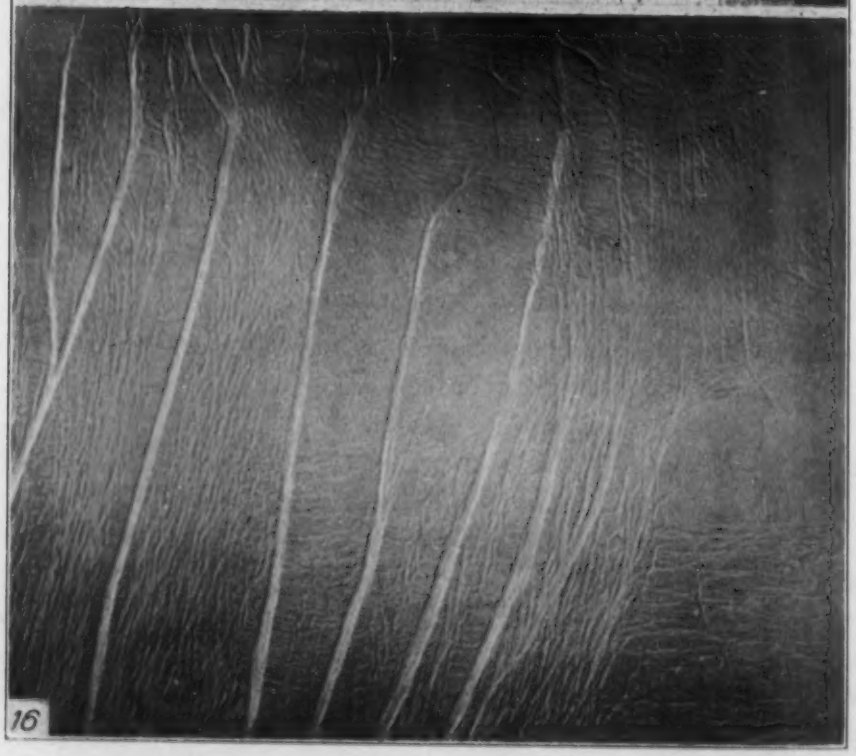


Fig. 15—Intergranular Corrosion Crack in Specimen Maintained Under Elastic Stress in Strong Alkali Salt Solution at About 210 Degrees Fahr. (100 Degrees Cent.). Magnification, × 125.

Fig. 16—Typical Stretcher Strains in an Automobile Stamping. (Specimen from Joseph Winlock.)

ductility or by some form of intergranular corrosive attack. As it happens, both of these effects are observed in metal which is particularly susceptible to strain-aging.

Many confirmatory tests are reported by German investigators in which very large impact specimens lose room temperature impact strength during aging while a corrosion test originated by some of the same investigators definitely confirms an intergranular attack in slightly worked metal after aging. As the corroding medium, a very strong solution (approximately 60 per cent $NaNO_3$) of an alkali salt is employed at about 212 degrees Fahr. (100 degrees Cent.). The specimen is an annealed bar bent to an approximate U-shape. Some permanent deformation is involved and the specimen is likewise under elastic stress during the corrosion test. In general one day's immersion in the hot solution will result in a complete fracture of the piece if it is of markedly strain-aging steel. Microscopic examination shows clearly that the corrosive attack is intergranular in character and leads to the conclusion that some material is definitely dissolved from the grain boundary, while the normal metal itself is substantially unattacked. Fig. 15 shows a photomicrograph at 125 diameters of one of these intergranular corrosion cracks. It may be assumed that the penetration rate is increased by the external stress upon the specimen and that conversely the local stress is highly concentrated at the grain boundaries where corrosive attack has already removed a thin film of material to form a notch. The test thus falls into the class of increasing rate phenomena.

The most probable explanation of this test appears to be in the precipitation, during aging, of a myriad of minute oxide particles in the grain boundaries which under the action of an alkali salt form a soluble ferrate. The removal of this almost continuous dispersion of oxide permits rupture of the metal along the grain boundaries. A wide variety of alkali compounds, particularly the hydroxide, are said to cause this intergranular attack but, for reasons not immediately apparent, the nitrate seems to be especially rapid in action. Metal which has been even a little cold-worked, as in bending the specimen, is attacked more rapidly than the wholly undeformed, annealed steel and it seems quite possible that the slip planes set up in the deformation may assist in the migration of the oxygen (in supersaturated solid solution) to the grain boundary. Severe cold work would probably prevent the specifically intergranular attack and cause only a mild general attack.

If this explanation be correct it is easy to see why steel which shows strain-aging is likewise said to be susceptible to the so-called "alkali embrittlement" or "caustic embrittlement" which is found to occur in boilers. The alkali salt in the boiler feed water may easily concentrate in certain isolated inaccessible crevices in the boiler to a point at which, in time, the action described above may occur. The non-aging steel first manufactured was primarily intended for use in boilers, wherein the stress necessary for the slow attack is supplied by the steam pressure and, as has been shown, the modern operating temperature is sufficient to bring about rapid aging in the moderately worked metal near joints and punched holes. It should be borne in mind that mere aging, i.e., the precipitation of a compound upon slip bands or grain boundaries would not in itself greatly reduce the strength, or perhaps even the ductility, of a steel, as measured at boiler temperature, to any significant degree but on the other hand the slow attack of the concentrated boiler water from some sources may impair the boiler steel.

It is interesting to note that whereas most low carbon steels are found to be at least somewhat subject to the general phenomenon of caustic embrittlement, a 12 per cent chromium steel appears immune. In this steel the amount of oxygen which could be dissolved at high temperature and re-precipitated at low temperature must be vanishingly small (as may be deduced from the difficulty of reducing chromium oxide and from its furnace reactions). This circumstance would lead one to predict its freedom from strain-aging if oxygen be the element involved, as seems most probable. A high silicon steel, if it were otherwise suitable, would likewise be expected to be free from strain-aging and this intergranular failure of "caustic embrittlement." The severity of embrittlement in boiler construction is often minimized by removing the moderately cold-worked metal from the vicinity of punched rivet holes, etc., a practice well explained by the habits of strain-aging.

Stretcher Strains and Aging

In the introduction and later under the discussion of etching effects occasion has arisen to mention the unique property of *annealed* low carbon steel to yield abruptly and markedly under stress and then to continue such local deformation under a stress distinctly lower than that required to cause the first plastic flow. The photograph of Fig.

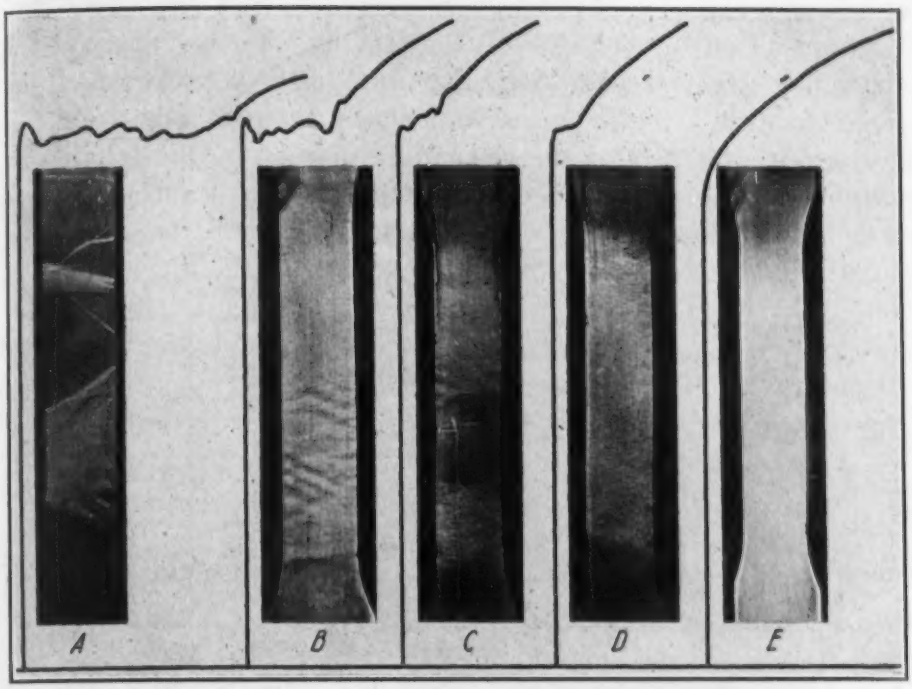


Fig. 17—Five Stress-strain Curves Showing Different Amounts of Elongation at Yield Point, Together with Photographs of the Corresponding Tensile Specimens. Yield Point Elongations Were as Follows: A—9 Per Cent; B—3.5 Per Cent; C—1.6 Per Cent; D—1.0 Per Cent; E—0 Per Cent (Kenyon and Burns).

12a illustrates the nature of the specimen after load has been applied. The appearance of metal in which certain isolated zones have suddenly become elongated or upset (depending upon the nature of the stress, tension or compression) is characteristic and the lines or bands of deformed metal were named, after their discoverer, Lüder's lines. Lüder described the phenomenon in 1860. The nature of the stresses set up in the deep drawing and stamping operations seem particularly suited to develop these bands of relief or intaglio in the sheet or strip metal and the name "stretcher strains" is now generally applied to the markings, or, in some shops, the designation is "worms." The markings may be attended by a change in gage of as much as 10 per cent of the metal thickness, plus or minus, depending upon the stress, and in automobile body stampings, are regarded as particularly objectionable; clearly, severe grinding must be applied to remove them. A typical example of stretcher strains is shown in the automobile body section of Fig. 16. The mode of their formation may best be understood by an examination of the stress-strain diagram of a susceptible specimen in the tensile test as in Fig. 17,

in which the strain markings are correlated with the stress-strain diagrams (Kenyon and Burns). It will be seen that the load falls somewhat after reaching the limit for elastic behavior, and then varies erratically until some few per cent elongation has occurred. During the first part of the elongation, marked by the roughly flat portion of the stress-strain diagram, the metal at some part of the specimen is yielding in bands, which ultimately fill the entire gage section; thereafter the smoothly curved part of the diagram is pro-

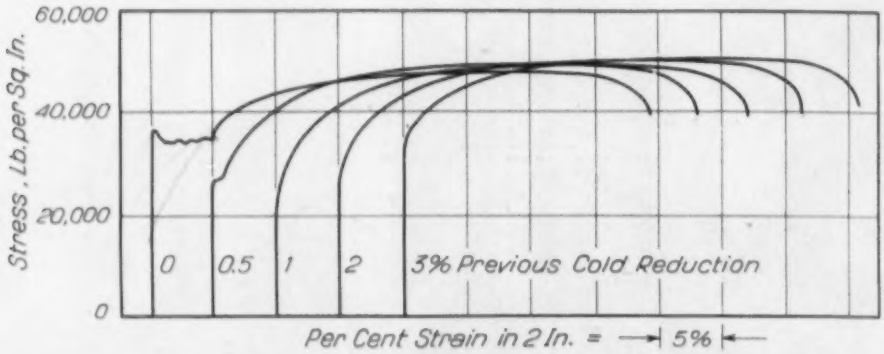


Fig. 18—Stress-strain Curves of Mild Steel Sheets Subjected to the Indicated Amounts of Cold Work Prior to Tensile Testing. Note Absence of Marked Yield Point in Materials Subjected to About 1 Per Cent or More Cold Reduction. (Griffis, Kenyon and Burns.)

duced. The susceptibility of a material to stretcher-straining is roughly measurable in terms of the per cent elongation which occurs by this initial low stress yielding.

For many years it has been recognized that cold working removed this yielding quality from low carbon steel and the susceptibility to stretcher strains. Clearly, the cold rolling produces some deformation in a positive manner in every grain and the metal then is already in the second state of the deformation diagram when it goes into test or under the press. The gradual loss of the marked yielding behavior by increasing cold work is shown in Fig. 18 (Griffis, Burns and Kenyon) by means of stress-strain diagrams. As a matter of fact the necessary cold work is often applied by means of roller levelling which suffices to induce the required slip bands in the grains without much altering the gage of the plate or strip and which causes a minimum change in hardness.

But the effect of the cold work is not permanent and, during storage, the metal reverts, insofar as stretcher strains are concerned, to the "annealed" condition except when the cold work applied to prevent them is so severe as to cause undesirable hardening. The rate

at which the stretcher strain condition is regained is, apparently, inversely proportional to the severity of the deformation. But this rate is also dependent upon the temperature of the metal during the interval following the light rolling or roller levelling, and this circumstance immediately calls to mind the other manifestations of

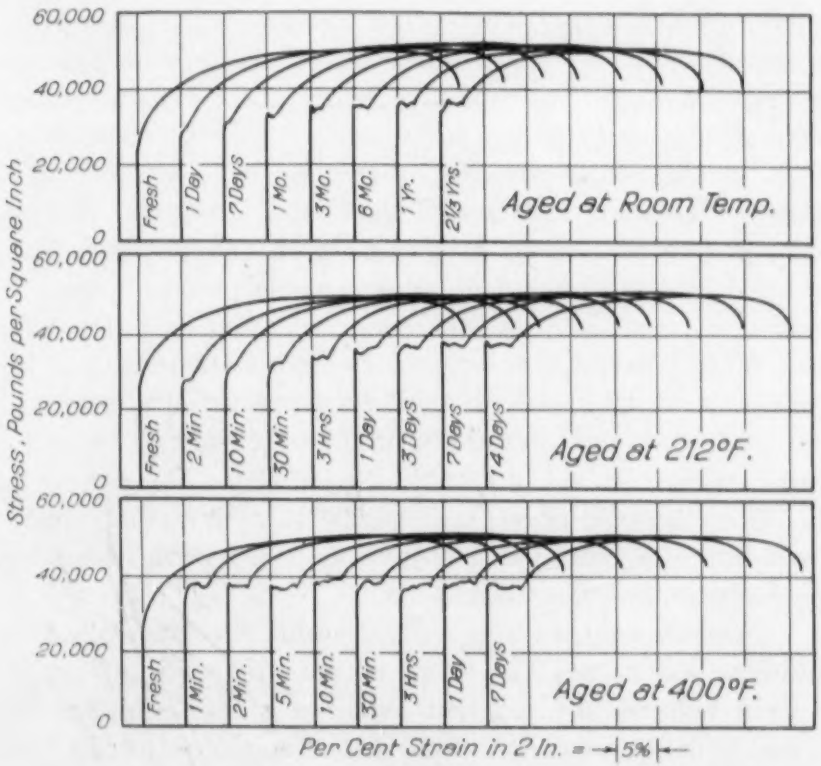


Fig. 19—Stress-strain Curves of Mild Steel Sheets Cold-rolled 1 Per Cent and Aged for the Indicated Times at Three Different Temperatures, Showing the More Rapid Return of the Marked Yield Point at Higher Aging Temperatures. (Griffis, Kenyon and Burns.)

aging. For example, a certain arbitrarily chosen degree of susceptibility to stretcher straining may be regained after a cold working treatment of 1 per cent reduction about as follows:

Temperature	Time Interval
70 degrees Fahr. (20 degrees Cent.)	526,000 minutes (1 year)
212 degrees Fahr. (100 degrees Cent.)	180 minutes (3 hours)
400 degrees Fahr. (205 degrees Cent.)	1 minute

Fig. 19 shows the gradual re-acquisition of stretcher strain behavior, as reflected in the stress-strain diagram, in a uniformly worked steel during aging at three temperatures (Griffis, Burns and Kenyon).

Thus it is to be seen that the cold-worked metal, without heating into the temperature range ordinarily associated with annealing, has nevertheless been able to re-acquire at least this one characteristic of annealed low carbon steel.

Simultaneously with the return of the marked yield condition, the already described age-hardening following cold work takes place. The mere fact that the stretcher strain behavior is gradually restored, in a material which was freed of this susceptibility, over a period of time which diminishes with elevated temperature maintained during the interval, although strongly suggestive of the various strain-aging processes would not necessarily prove that it is a *result* of age-hardening. It is extraordinarily significant, however, that steels which have been deoxidized in a manner to eliminate substantially all the age-hardening after cold work are also practically free from the return of stretcher strain behavior; and this leads one to contemplate some possible connection between the two sorts of aging (i.e., return of stretcher straining and hardening by strain-aging).

To establish beyond question a proof of a common cause is not at present possible but one might reason somewhat along these lines:

1. Even the most nearly pure iron shows the marked yield type of stress-strain diagram in the annealed state along with the oxygen-bearing commercial low carbon steels.

2. Moderate cold working either in rolls, levelling rolls, or in a wire-drawing die causes the metal to pass through this stage of initial yield without any external evidence of the stretcher strain effect, which in free tension would have been observable. At the same time this cold work, which eliminates stretcher strains, conditions the metal for precipitation-hardening which begins to take place at once in commercial oxygen-bearing metal but not in oxygen-free metal as discussed further under non-aging steels.

3. Concurrently with the hardening and strengthening of the metal due to strain-aging the return to stretcher strain behavior occurs, which in effect means a partial recovery of the behavior of "annealed" metal. Now one may suppose that (1) very little real annealing after cold work can occur at temperatures as low as 200 degrees Fahr. (100 degrees Cent.), and (2) even if such incipient annealing did occur it would occur similarly in metal free from precipitation and in metal subject to precipitation. Nevertheless, where precipitation hardening occurs, the stretcher strains reappear in the tensile test and where precipitation does not occur, as in the

low oxygen iron, the metal retains the cold-worked condition for a long time, with its freedom from stretcher strains.

4. To continue along this line of reasoning one may then postulate that it is a distributed pattern of microscopic stresses set up during the mild cold working which inhibits stretcher strains and that the precipitation of a compound upon the slip-planes suffices to relieve these stresses and thereby to restore the stretcher strain condition without, however, softening the metal as annealing would have

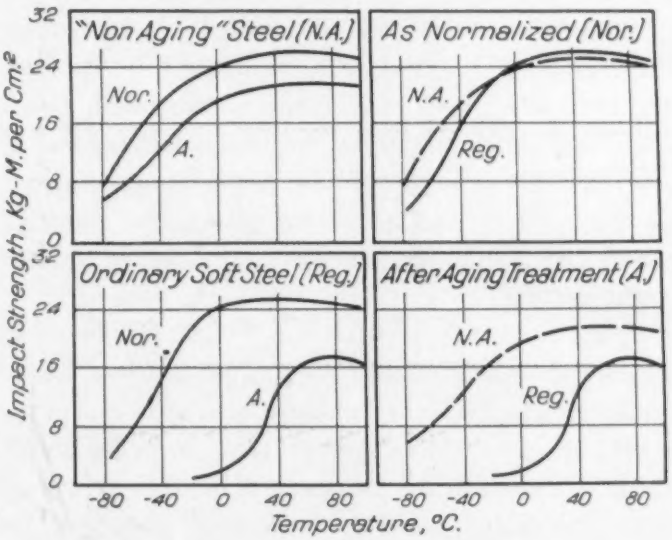


Fig. 20—The Comparative Impact Strength at Various Temperatures of Ordinary Open-hearth Steel (Reg.) and "Non-Aging" Steel (N-A.) in Both the Normalized Condition (Nor.) and After Aging Treatment (A.).

Specimens: 15 x 30 x 160 mm., 120 mm. Between Supports. Notch, 4 mm. Wide, 15 mm. Deep, Round Bottom.

Aging Treatment: 10 Per Cent Elongation Cold Followed by One-half Hour at 250 Degrees Cent. (480 Degrees Fahr.) (Fry).

done. Actually, as repeatedly shown, the metal is mildly hardened by precipitation. In support of this hypothesis one may only suggest that the forces of chemical nature which induce precipitation may be of high magnitude (indeed they definitely appear strong) and if the rearrangement involved in the precipitation could supply a trace of transient mobility in the metal the relief of stresses might be expected to occur. Another very similar mechanism suggests itself. If volume changes occur, the attendant readjustments might likewise directly accomplish the relief of the stresses which prevent stretcher strains.

One may only say that the means of producing steels which do

not age-harden nor lose much ductility under the conditions of strain-aging as shown in Fig. 20, are the same in trend as applied to prevent the product from rapidly recovering its stretcher straining tendencies. There is no completely sound basis for concluding that the basic causes are the same for both changes, but the probability is that they are both intimately related to a precipitation of an iron compound. It is perhaps significant that steels which are satisfactorily non-aging in the commercial sense may still exhibit some slight gain in hardness; serious blue-brittleness and possibly caustic embrittlement are substantially eliminated even though careful hardness studies may still reveal a trace of age-hardening as shown in Fig. 21.

Since the carbon-aging which occurs in annealed, normalized or other unworked steel may easily be circumvented by the process of pre-aging described above, it might be expected that any steel may also be pre-aged with respect to strain-aging. In principle this is true; whether or not it may be commercially feasible to so treat steel is not at present certain.

The pre-aging for this type of aging is accomplished by working the metal cold and then heating to some temperature of rapid precipitation and coalescence. This treatment succeeds in putting away some portion of the dissolved oxygen in the form of a harmless particle distribution. The trouble, however, with this treatment is that the action is not complete; another succeeding cold working operation appears to re-condition new metal for precipitation and there is unfortunately still some oxygen to be precipitated. Accordingly the operation of cold-working and re-heating may have to be repeated several times to be effective. It is safe to predict, however, that sheet or strip which has been produced by means of a great deal of cold-rolling, if re-heated to a suitable temperature (e.g., 650-700 degrees Fahr., 340-370 degrees Cent.) during process, will be noticeably superior to ordinary sheet metal with respect merely to the strain-aging phenomena.

Oxygen Responsible for Strain-Aging

The accumulated evidence favoring the view that the precipitation of an iron compound upon the slip bands of cold-worked steel is the cause of the various effects of strain-aging naturally raises the question of which element in the steel combines with the iron to form the dispersed particles. Since the effect is well marked even in low

metalloid steels the responsibility might well fall upon any of the elements present in low concentration with the iron. Thus at a glance, sulphur, phosphorus, nitrogen, carbon and oxygen are all suspects; even hydrogen has not entirely escaped suspicion although it is not now regarded as even a possible contributor.

Of these it now appears that both phosphorus and nitrogen have too great solubility in iron even at low temperature to precipitate from such dilute solutions as are represented by most low carbon strain-aging steel.

Rather less is known of sulphur but since no investigator has found any solubility of sulphur in alpha iron it may be safe to re-

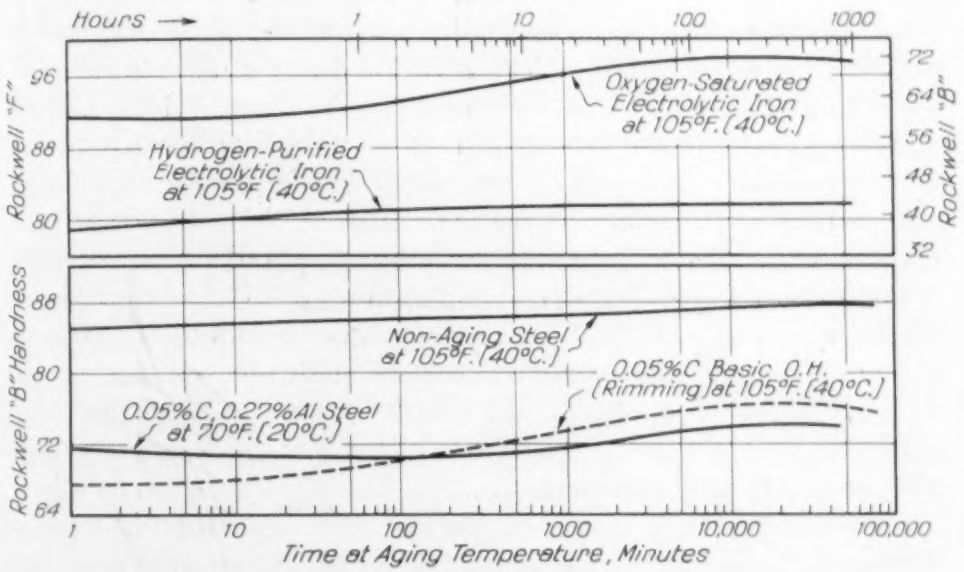


Fig. 21—Upper Block—Hardness of O_2-Saturated Electrolytic Iron, No. 4, and H_2-Purified Electrolytic Iron as Strain Aged at 105 Degrees Fahr. (40 Degrees Cent.); Pre-aged Before Cold Deformation.

Lower Block—Hardness of Non-aging Steel No. 11, and Rimming Basic O. H., No. 10, as Strain Aged at 105 Degrees Fahr. (40 Degrees Cent.); Also 0.27 Per Cent Al Steel, No. 3, as Strain Aged at 70 Degrees Fahr. (20 Degrees Cent.); All Pre-aged Before Cold Deformation.

gard that it has an unusually low solubility and hence a more remote chance of causing age-hardening than has oxygen and carbon. Furthermore, aging does not appear to vary greatly in intensity with sulphur content even up to and including such amounts as are present in screw stock.

The rather simple and forthright behavior of carbon in causing aging has already been discussed; by virtue of its change in solubility from about 0.05 per cent at 1325 degrees Fahr. (720 degrees Cent.)

to perhaps 0.005 per cent at 200 degrees Fahr. (100 degrees Cent.) and its faculty of precipitating generally throughout the whole of a ferrite grain, its contribution to aging may be fairly clearly set forth. By the same token its precipitation may be induced to proceed to substantial completion after which coalescence permits a stabilization which eliminates carbide precipitation from the question of strain-aging.

There remains then, of the suspected elements, oxygen whose solution and re-precipitation might account for strain-aging. In support of this indictment is the very significant circumstance of the non-aging steels being manufactured by a practice which would primarily be expected to reduce the dissolvable oxygen to vanishingly small concentration. A few studies on the degree of hardening occurring during aging in several special metals serves to add still more weight to the case against oxygen.

The uppermost curve in Fig. 21 shows the hardening response of a carbon-free, high oxygen iron which clearly indicates that oxygen is capable of causing strain-aging. Indeed, the response of this metal is comparable with that of the basic open-hearth rimming steel in the lower block of Fig. 21. The three metals of the lower block, due to their carbon content, were examined by Rockwell B hardness while the two very pure metals were so soft as to require the special Rockwell F scale for study. In contrast to these oxygen-bearing metals the hydrogen-purified electrolytic iron and the aluminum alloy show very little age-hardening.

This comparison seems to narrow the responsibility rather sharply to the oxygen of the metal, and unless more decisive subsequent experimentation permits other conclusions to be drawn, one may be justified in regarding oxygen as almost certainly the element with which the iron forms that particular compound which is located in the slip bands and hence characterizes strain-aging.

Conclusions

The evidence presented in the preceding pages had led us to the conclusion that the various aging effects in low carbon steel result from precipitation phenomena of two types:

A. *Carbon-aging.* In annealed steel iron carbide is precipitated from ferrite, supersaturated with respect to carbon, in a random manner throughout the grains.

B. *Strain-aging.* Ferrite seemingly supersaturated with oxygen, rejects an iron-oxygen compound in the slip bands of cold-worked grains and is thereby hardened.

Both precipitation hardening reactions may often progress simultaneously but can be studied separately.

An "over-aging" or "pre-aging" treatment (equilibration) is prescribed for the former and means of minimizing the effects of strain-aging are discussed.

ACKNOWLEDGMENTS

The authors wish to express their indebtedness for very considerable assistance in the work described here: to Dr. John Johnston, Director of Research, for his guidance and sympathetic criticism, and to Mr. W. S. N. Waring, formerly of the authors' laboratory, for his careful and painstaking work involving many thousands of tests upon variously aged specimens.

Selected Bibliography

1. C. E. Stromeyer, "The Aging of Mild Steel," *Journal,* Iron and Steel Institute, Vol. I, No. 73, 1907, p. 200.
2. B. Baumann, "Sprödigkeit von Flusseisen als eine Folge der Erwärmung gequetschten Materials," *Zeitschrift des Vereines deutscher Ingenieure,* Vol. 59, 1915, p. 628.
3. Merica, Waltenberg and Scott, "Heat Treatment of Duralumin," *Bulletin,* American Institute of Mining and Metallurgical Engineers, June 1919. Also United States Bureau of Standards, *Scientific Paper No. 347,* Nov. 15, 1919.
4. F. Fettweis, "Ueber die Blaubrüchigkeit und das Altern des Eisens," *Stahl und Eisen,* No. 39, 1919, p. 1 and 34.
5. A. Fry, "Kraftwirkungsfiguren in Flusseisen, dargestellt durch ein neues Aetzverfahren," *Kruppsche Monatshefte,* Vol. 2, July 1921, p. 117.
6. Strauss and Fry, "Rissbildung in Kesselblechen," *Kruppsche Monatshefte,* Vol. 2, 1921, p. 126.
7. M. Moser, "Zur Gesetzmässigkeit der Kerbschlagprobe," *Kruppsche Monatshefte,* Vol. 2, 1921, p. 225, and *Stahl und Eisen,* No. 42, 1922, p. 90.
8. B. Baumann, "Kesselschaden," *Zeitschrift Bayerischer Revisionsverein,* Vol. 27, 1923, p. 132.
9. M. Moser, "Was Haben wir an der Kerbschlagprobe," *Stahl und Eisen,* No. 42, 1923, p. 935.
10. B. Baumann, "Neue Aeusserungen zur Laugenfrage aus Amerika," *Zeitschrift Bayerischer Revisionsverein,* Vol. 27, 1923, p. 151.
11. R. Mailänder, "Einfluss der Probenbreite auf die Kerbzähigkeit von Flusseisen," *Kruppsche Monatshefte,* Vol. 5, 1924, p. 16, and *Stahl und Eisen,* No. 45, 1925, p. 392 and 1607.

12. B. Baumann, "Ueber eine neue Auffassung hinsichtlich der Wirkung des Speisewassers auf die Entstehung von Kesselschäden," *Zeitschrift Bayerischer Revisionsverein*, Vol. 29, 1925, p. 165.

13. R. Mailänder, "Das Aehnlichkeitsgesetz bei der Kerbschlagprobe," *Kruppsche Monatshefte*, Vol. 7, 1926, p. 217, and *Stahl und Eisen*, No. 46, 1926, p. 1752.

14. A. Fry, "Das Verhalten der Kesselbaustoffe im Betrieb," *Kruppsche Monatshefte*, Vol. 7, 1926, p. 185.

15. W. P. Sykes, "The Iron-Tungsten System," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 68, 1926, p. 968.

16. F. Körber and A. Pomp, "Rissbildungen und Anfressungen an Dampfkesselementen," *Mitteilungen aus dem Kaiser-Wilhelm Institut für Eisenforschung*, Vol. 8, 1926, p. 135, and *Korrosion und Metallschutz*, Vol. 3, 1927, p. 97.

17. B. Baumann, "Kesselschäden und Ihre Ursachen," *Wärme*, Vol. 50, 1927, p. 551.

18. F. Körber and Anton Pomp, "Vergleichende Untersuchung über das Verhalten von unlegierten und legierten Kesselblechen bei erhöhten Temperaturen und hinsichtlich Alterung und Rekristallisation," *Mitteilungen aus dem Kaiser-Wilhelm Institut für Eisenforschung*, Vol. 9, 1927, p. 339.

19. O. Bauer, "Untersuchung einer gerissenen Schiffskesselplatte," *Mitteilungen aus dem Materialprüfungsamt zu Berlin-Dahlem*, Vol. 35, 1927, p. 194.

20. A. Fry, "Die Frage des wenig alterungs-empfindlichen Flusseisens," Reprint, *Zeitschrift Bayerischer Revisionsverein*, 1928.

21. K. Daeves, "Bericht über die siebte Tagung des Allgemeinen Verbandes der deutschen Dampfkesselüberwachungs-Vereine," *Stahl und Eisen*, No. 48, 1928, p. 1218.

22. F. Fettweis, "Die Kerbschlagprobe, Entwicklung und Kritik," Report No. 143 of the Material Committee of Vereines deutscher Eisenhüttenleute and Archiv Eisenhüttenwesen, Vol. 2, 1928-29, p. 625.

23. O. Bauer, "Flusstähle mit geringer Alterungseigenschaft," *Zeitschrift Bayerischer Revisionsverein*, Vol. 32, 1928, p. 23, and 41; *Mitteilungen aus dem Materialprüfungsamt zu Berlin-Dahlem*, 1929, Reprint 5, p. 12

24. F. Nehl, "Alterungserscheinungen an Dampfkesseln und ihre Vermeidung," *Zeitschrift Bayerischer Revisionsverein*, Vol. 32, 1928, p. 315 and 324; *Stahl und Eisen*, No. 49, 1929, p. 472.

25. W. Köster, "Der Einfluss einer Wärmebehandlung unterhalb A_1 auf die Eigenschaften des Technischen Eisens," *Archiv Eisenhüttenwesen*, Vol. 8, Feb. 1929.

26. A. Pomp and P. Badenheuer, "Schadenfälle an Dampfkesselelementen," *Mitteilungen aus dem Kaiser-Wilhem Institut für Eisenforschung*, Vol. 11, 1929, p. 185.

27. A. Krüger, "Die Alterung der Werkstoffe," *Archiv Eisenhüttenwesen*, Vol. 3, 1929-30, p. 721.

28. Anonym, "Untersuchung von Kesselschäden," *Zeitschrift Bayerischer Revisionsverein*, Vol. 34, 1930, p. 167.

29. O. Schwarz, "Sprödigkeitserscheinungen bei Stahl," *Maschinenbau*, Vol. 9, 1930, p. 471.

30. M. Ulrich, "Werkstoffragen des heutigen Dampfkesselbaues," Verlag J. Springer, 1930, p. 35.

31. M. Ulrich, "Amerikanische Versuche über 'embrittlement of boiler plate' und deutsche Vergleichsversuche," *Zeitschrift Bayerischer Revisionsverein*, Vol. 34, 1930, pp. 13, 34, 49, 64, 88, 98, 129.

32. M. Ulrich, "Sonderstähle für den Kesselbau," *Archiv für Wärmewirtschaft*, Vol. 11, 1930, p. 11.

33. W. Köster, Ueber die Eigenschaftsänderungen der Eisen-Stickstoff Legierungen durch Abschrecken und Anlassen unterhalb A_1," *Archiv Eisenhüttenwesen*, Vol. 8, Feb. 1930.

34. H. Jungbluth, "Werkstoffe für den Dampfkesselbau," *Kruppsche Monatshefte*, Vol. 11, July 1930, p. 177.

35. R. F. Mehl, "The Aging of Iron and Steel," Lecture before Ontario Research Foundation, Oct. 31, 1930, Toronto, Canada.

36. W. Köster, "Zur Frage des Stickstoffs im Technischen Eisen," *Archiv Eisenhüttenwesen*, Vol. 10, Dec. 1930, p. 637.

37. W. Köster, "Beitrag zur Kenntnis des Systems Eisen-Stickstoff," *Archiv Eisenhüttenwesen*, Vol. 11, 1930-31, p. 537.

38. J. Reschka, "Beitrag zur Frage des Sauerstoffs im Eisen," Doktor-Ingenieurs Dissertation, Technische Hochschule Braunschweig, June 1931, (Stahldruck, Dortmund).

39. Thomas Dockray, "Sheet Steel, Its Drawing Quality," METAL PROGRESS, American Society for Steel Treating, Vol. 20, No. 4, 1931, p. 54. (A paper read at the American Society for Steel Treating Convention in Boston, Sept., 1931.)

40. O. Bauer, "Ueber die Ursachen von Dampfkesselschäden," Mitt. V.O.B., 1931, No. 32, (Sonderdruck), p. 89.

41. H. Jungbluth, "Alterungskerbzähigkeit und Kraftwirkungsfiguren-Aetzung," *Kruppsche Monatshefte*, Vol. 12, 1931, p. 106.

42. H. Jungbluth and H. Müller, "Warmfeste und Korrosionsbeständige Stähle für den Dampfkesselbau," *Kruppsche Monatshefte*, Vol. 12, 1931, p. 179.

43. Joseph Winlock and A. E. Lavergne, "Stretcher Strains Depend Upon Speed of Draw, METAL PROGRESS, American Society for Steel Treating, Vol. 20, No. 3, 1931, p. 90.

44. H. von Kochritz, "Ueber den zeitlichen Verlauf der Alterung weichen Stahles und über die Alterung von Stählen verschiedener Herkunft," *Mitteilungen aus dem Forschungs Institut*, Verlag Stahlwerke A. G. Vol. 2, No. 9, 1932.

45. W. Köster, H. von Kochritz and E. Schultz, "Zur Kenntnis der Form der Spannungs-Dehnungs-Kurven auf Grund der Messung des zeitlichen Verlaufes der Alterung weichen Stahles," *Archiv Eisenhüttenwesen*, Vol. 2, 1932-33, p. 55.

46. R. O. Griffis, R. L. Kenyon, R. Burns, "The Aging of Mild Steel Sheets," Yearbook, American Iron and Steel Institute, 1933, p. 142.

47. R. L. Kenyon and R. S. Burns, "Autographic Stress- Strain Curves of Deep-Drawing Sheets," TRANSACTIONS, American Society for Steel Treating, Vol. 21, No. 7, 1933, p. 577.

48. Joseph Winlock and A. E. Lavergne, "Some Effects of the Amount and Rate of Deformation on a Low-Carbon Strip Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 21, No. 2, 1933, p. 109.

49. E. B. Wittemore, "Age Hardening in Low Carbon Strip Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 21, No. 6, 1933, p. 571.

50. J. Jungbluth and H. Berndt, "Die Kerbschlagprobe zur Prüfung Mechanischer Alterung," Kruppsche Monatshefte, demnächst.

51. A. Hayes and R. O. Griffis, "Non-Aging Iron and Steel for Deep-Drawing," *Metals and Alloys*, Vol. 5, No. 5, 1934, p. 110.

52. B. W. Gonser and L. R. Van Wert, "The Age Hardening Characteristics of Some Copper-Nickel-Silicon Alloys," Part I, *Metal and Alloys*, Vol. 5, No. 11, 1934, p. 251; Part II, Vol. 5, No. 12, 1934, p. 281.

53. J. L. Burns, "Premature Precipitation in Supersaturated Solutions, with Special Regard to Austenite," (Part I) TRANSACTIONS, American Society for Metals, Vol. 22, No. 8, 1934, p. 728.

54. R. H. Harrington, "The Present Status of Age-Hardening," TRANSACTIONS, American Society for Metals, Vol. 22, No. 6, 1934, p. 505.

55. J. L. Burns, "Classification of Alpha Iron-Nitrogen and Alpha Iron-Carbon as Age-Hardening Alloys, *Metals Technology*, American Institute of Mining and Metallurgical Engineers, August 1934, Technical Paper 556.

56. John T. Norton, "Solubility of Copper in Iron and Lattice Changes during Aging," *Metals Technology*, American Institute of Mining and Metallurgical Engineers, December 1934, Technical Paper 586.

57. M. L. Fuller and R. L. Wilcox, "Studies of Phase Changes during Aging of Zinc-Alloy Die-Castings," *Metals Technology*, American Institute of Mining and Metallurgical Engineers, September 1934, Technical Paper 572.

58. Paul D. Merica, "Precipitation Hardening," METAL PROGRESS, American Society for Metals, Vol. 27, No. 1, 1935, p. 31.

59. Paul D. Merica, "Some of the Alloys that Age-Harden," METAL PROGRESS, American Society for Metals, Vol. 27, No. 3, 1935, p. 46.

Correspondence

From Albert Portevin, "Similarities Between Abnormality and Aging," METAL PROGRESS, American Society for Metals, Vol. 26, No. 3, 1934, p. 38.

From C. H. M. Jenkins, "Proper Terms to Describe Age-Hardening," METAL PROGRESS, American Society for Metals, Vol. 25, No. 6, 1934, p. 47.

DISCUSSION

Written Discussion: By Dr. R. N. Arnold, Commonwealth Fellow, University of Illinois, Urbana, Illinois.

The aging of low carbon steel which follows rapid cooling from high temperatures is a phenomenon on which the writer has conducted quite extensive research. The study of this particular type of aging, however, appears incomplete without an investigation of the changes in impact properties with which it is accompanied. Had the authors of the present paper been in possession of such impact data they might have been in a position to put forward a more detailed explanation of the possible causes of aging in low carbon steel. Reference may be made to a paper by Lea and Arnold[1] describing research conducted at the University of Sheffield, England on the embrittlement of low carbon steel. This paper, it is believed, contains a few new observations of the phenomenon of aging in steel and it is in the light of these that the writer wishes to put forward a theory of aging applicable to low carbon steel. The

[1]Lea and Arnold, "The Embrittlement of Low Carbon Steel," *Proceedings*, Institute of Mechanical Engineers, 1934, p. 299.

theory is not entirely new; casual explanations by other workers have indicated such possibilities, though few, if any, have attempted a detailed survey of the processes involved.

It seems necessary to state first some of the basic facts about the aging of steel which have been established by experiment. The following summary contains data which refers to a 0.14 per cent carbon steel used by the writer.

(1) Increased hardness, tensile strength, and fatigue limit with decreased ductility, and resistance to impact are the results of aging at room temperature after rapid cooling from temperatures between 600 and 700 degrees Cent. (1110-1290 degrees Fahr.).

(2) In general the lower temperatures of aging produce the greater hardening. The time interval for reaching maximum hardness decreases with increase of aging temperature. For the higher temperatures the hardening is followed in time by softening after which carbide precipitation can be observed.[2] In view of the long time taken in aging the above cannot be verified for low temperatures.

(3) A piece of steel aged for say six months in the manner described in (1) will decrease in hardness by about 10 per cent, when heated at 100 degrees Cent. for 10 minutes. If heating is continued the hardness again rises and finally softening sets in.

(4) With an aging temperature of 100 degrees Cent. age-hardening (measured at room temperature) occurs followed by softening. This particular hardening is unaccompanied by brittleness (as measured by impact), but unless aging at 100 degrees Cent. is continued for more than 3½ hours age embrittlement will again assert itself at room temperature in a degree varying inversely with the time of aging at 100 degrees Cent.

Of the above statements (1) and (2) give effects generally accepted by all investigators and to which the authors make reference in their paper. To supplement statements (3) and (4) reference may be made to observations on the age-hardening of duralumin by other workers. Gayler and Preston[3] have shown that when duralumin, which has been aged at room temperature, is treated at 200 degrees Cent. softening occurs almost instantaneously, and is followed by a second phase of age-hardening. Portevin[4] has also recorded significant results. He has shown that alloys of the duralumin class when aged at low temperatures, do not exhibit the accepted evidences of precipitation, in fact, the increased hardness is associated with a variation in volume which is the reverse of that which should accompany precipitations. Above a certain temperature the aging process becomes normal, and is in agreement with the precipitation hardening theory.

From the above statements it seems evident that there are two distinct processes involved in the aging of low carbon steel (a) aging which produces hardness accompanied by brittleness and (b) aging which produces hardness unaccompanied by brittleness. In studying such aging processes it is necessary

---

[2]A. A. Bates, "Aging of Low Carbon Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 449.

[3]Gayler and Preston, "The Age-hardening of Some Aluminum Alloys of High Purity," *Journal*, Institute of Metals, 1932, Vol. 48, p. 197.

[4]Portevin, "The Phenomena of Quenching and Tempering in Alloys," *Journal*, Institute of Metals, 1933, Vol. 51, p. 336.

to consider the atomic arrangement which exists in a low carbon steel immediately after rapid cooling from a high temperature. At such an instant the steel will consist mainly of ferrite (alpha iron) supersaturated with carbon. This is an interstitial solid solution the carbon atoms being situated within the alpha iron lattice. Now because of the excess carbon atoms the solution is not in a state of equilibrium and will attain to such a state in time by internal movements. Three possible ways of attaining equilibrium appear to present themselves.

(1) Excess carbon atoms may be expelled from the iron lattice and may unite to form a carbon lattice (graphite).

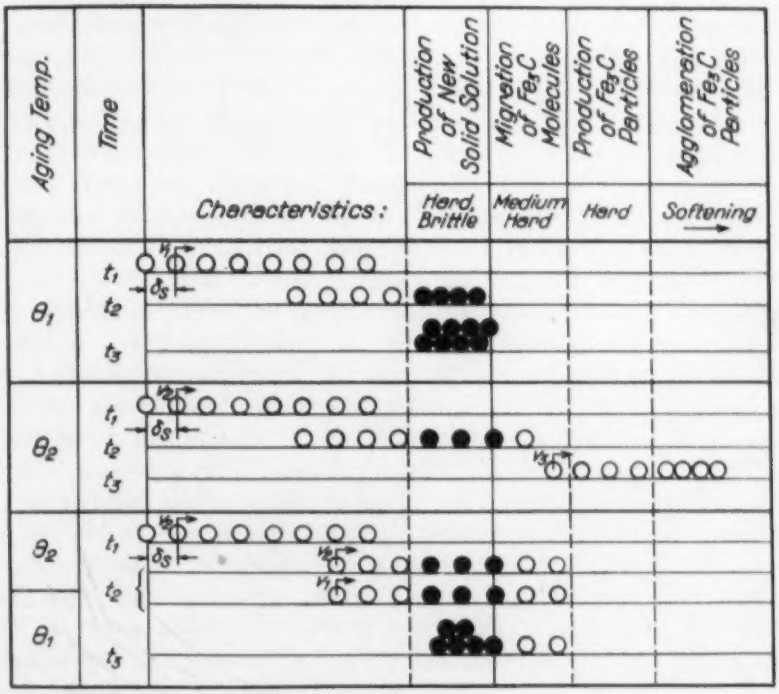
(2) Each excess carbon atom may combine with three adjacent iron atoms to form a molecule of Fe_3C.

(3) Each excess carbon atom may form a molecule of Fe_3C which will in turn migrate and unite with other molecules to form an Fe_3C lattice (cementite). Energy considerations show that the compound Fe_3C will form in preference to carbon precipitation.

It is suggested that processes (2) and (3) are those associated with the aging of mild steel and that (2) produces a new solid solution in which the molecules of Fe_3C formed from the excess carbon are substitutional, that is, they replace iron atoms in the lattice. The theory may now be developed along these lines with reference to observed phenomena. It is first suggested that the aging of low carbon steel at room temperature with its characteristic embrittlement is due to the formation of Fe_3C molecules the resultant structure being a mixture of two solid solutions. This would tend to agree with Portevin's[4] observation on duralumin of the decrease in volume during aging at low temperatures. The results obtained by aging at higher temperatures can be explained in terms of actual precipitation of the Fe_3C molecules to form a cementite lattice. The question may, however, be asked, "if one process merely precedes the other why does a short aging at a high temperature not produce similar results to a long aging at a low temperature?" The answer to this question depends on the assumption (which seems reasonable) that only a small percentage of the excess carbon atoms are at any instant in exactly the same stage of aging, in other words, all atoms do not commence the aging process at the same instant. A diagram may serve to illustrate this conception more clearly. For convenience the movements of atoms and molecules may be thought of in terms of small spheres set rolling along a line at various time intervals δt each being separated by a distance δs. Specific sections of this line may then correspond to specific internal atomic arrangement.

Suppose that internal equilibrium at an aging temperature θ_1, is attained by the excess carbon atoms producing a new solution of Fe_3C in alpha iron. The movements may then be pictured as in (a). As each atom in turn assumes equilibrium it will be observed that a building up process takes place as shown at times t_2 and t_3. Increased hardness and brittleness may therefore result due to the first type of aging. The movements for a higher aging temperature θ_2 are shown in (b). In this case since equilibrium does not occur until the Fe_3C molecules precipitate and form cementite particles then statistically only a small percentage of excess carbon atoms can exist in the brittle region at any instant t_3. The final hardening is then due to the second phase

of aging. If aging temperatures θ_2 and θ_1 are used in succession the results will be shown in (c). Let aging at θ_2 be followed at time t_2 by aging at θ_1. This will result in some degree of brittleness since all atoms which have not passed through the brittle range will build up as shown at time t_3. If time t_2 is large enough, however, all atoms will have passed through the first phase of aging, and subsequent brittleness cannot occur at temperature θ_1. By a similar



argument it may be shown that aging at θ_2 following prolonged aging at θ_1 should produce softening followed by hardening, which is exactly what experiment confirms.

In presenting the above the writer realizes that the theory is at the best a conjecture, but it is one which helps to visualize the submicroscopic movements which occur, even although the true explanation may be much more complicated. It has been assumed throughout that the aging is due to the presence of excess carbon in solution. This is an assumption which at present has not been satisfactorily confirmed. The writer, judging by the results of his own research, is inclined to the view held by the authors, that while nitrogen may play a conspicuous part in the aging, the main effects must be attributed to carbon. However, even if an element other than carbon is eventually found to play the major part, the above theory may still be valid by substituting the new element in place of carbon.

Written Discussion: By S. Epstein, Battelle Memorial Institute, Columbus, Ohio.

The authors are to be commended for a brilliant analysis of the problem of aging in iron and steel. They have shown that the hardness-time curves after quench aging differ markedly in type from the hardness-time curves

after strain aging. They have likewise shown that in the absence of carbon, quench aging does not occur even when the oxygen content is fairly high. On the other hand strain aging does occur in the absence of carbon—rather strongly in high oxygen material and more weakly in low oxygen material. They have, therefore, concluded that in ordinary commercial iron and steel quench aging is primarily due to carbon and that strain aging is primarily due to oxygen.

This makes a very helpful generalization, but in some respects the simplification has been carried too far. In the first place it is doubtful that a very sharp line of demarcation can be drawn between quench aging and strain aging. The two are more probably interrelated. Thus it is known that if the oxygen content is only high enough quench aging can occur even in the absence of carbon. Also, as Daniloff, Mehl, and Herty have just shown strong deoxidation of carbon steel makes the steel non-aging, both as to quench aging and as to strain aging. In the second place the nitrogen which may be present in commercial iron and steel, particularly Bessemer steel, cannot be entirely dismissed as playing a negligible rôle in aging.

The authors have stated that the solubility of nitrogen in steel at room temperature is greater than that present in ordinary steel, and that nitrogen, therefore, cannot give rise to precipitation and aging effects. Köster, however, who has done a lot of careful work on the subject places the solubility of nitrogen at room temperature at about 0.001 per cent nitrogen, which is less than that found in open-hearth steel and much less than that present in Bessemer steel. The writer has observed the presence of numerous precipitated nitride needles in open-hearth iron containing only 0.003 per cent nitrogen. Of course, it may be questioned whether this needle-like constituent is really iron nitride and not something else, iron oxide for example, yet the needles have generally been considered to be iron nitride. Indeed, the precipitated particles revealed after strain aging by Fry etching, have also been held to be iron nitride—and susceptibility to Fry etching has been recognized as one of the characteristics of aging steels. Fry etching reveals strain lines much more strongly in high nitrogen steels than in low nitrogen steels.

It is unfortunate that the authors have not included a high nitrogen Bessemer steel in the strain aging curves shown in Fig. 21. Moreover, the method of test, that of measuring the hardness after straining and aging was possibly not the best for bringing out the aging effect of nitrogen. It is known that steels vary not only in the degree in which they age harden after straining, but also in the degree to which they harden during the straining or cold working operation itself. This has been considered as an important factor in machineability. A steel which hardens readily and becomes embrittled under the action of the cutting tool should be easier to machine. It has been stated that the reason why Bessemer steel hardens more for a certain degree of cold work than open-hearth steel is that it has a higher nitrogen content. If this is so, then here is an important aging effect due to nitrogen.

However, the most prominent aging effect for which nitrogen may be responsible in part is the embrittlement following cold work and aging. This effect can only be observed in notched-bar or impact tests which the authors did not use in studying the effect of nitrogen. However, considerable evidence exists that higher nitrogen steels such as Bessemer steels are more susceptible

to embrittlement after cold work and aging than lower nitrogen steels. Indeed workers in Germany have recently concluded that nitrogen was much more effective in regard to this form of strain aging than oxygen.

The authors state they have obtained evidence that non-aging steels are less susceptible to caustic embrittlement than aging steel. In view of the contradictory evidence which exists on this point, the inclusion in the paper of the actual data obtained would have been of interest. The German workers have repeatedly claimed that non-aging steel is less susceptible to caustic embrittlement than aging steel. On the other hand Straub in this country, several years ago found early samples of Izett non-aging steel to be as susceptible to caustic embrittlement as aging steel. The explanation may be that Straub's Izett samples were in the as-rolled condition, not normalized, and that even a non-aging steel must be made fine-grained by normalizing before it will withstand caustic embrittlement. This is mentioned here because it brings in another important variable in both quench and strain aging, that of grain size, in which Daniloff, Mehl, and Herty have given some interesting data.

It would be helpful if the aging phenomena could be simplified to the extent indicated in the paper. Perhaps further work will show that it can indeed be so simplified. The evidence available at present, however, does not seem fully to support the view that the cause of quench aging is entirely different from that of all types of strain aging, and that quench aging is due solely to carbon and strain aging solely to oxygen. Instead in commercial steel these effects appear to be interrelated. For example the tendency of carbon to cause quench aging may be affected by the presence of oxygen which very likely changes the solubility of carbon in ferrite. Likewise certain phases of strain aging may be due in part to carbon or nitrogen, or even phosphorus. The latter for example does not of itself give rise to aging effects but it may cause carbon or nitrogen to do so by changing their solubility in ferrite. This sets up an unpleasantly complicated picture which will no doubt be greatly clarified by further work in this fascinating field. On the other hand, here may be another of the many instances, where nature has not taken sufficient pains to make things simple.

Written Discussion: By N. A. Ziegler, 821 Holland Ave., Wilkinsburg, Pa.

The great amount of experimental work and its excellent presentation speak for themselves and, although deserve full admiration, need very little additional comment.

I do not quite agree with the authors' statement that "coersive force (magnetic) . . . . while undoubtedly a varient with aging, is not directly a measure of its progress." Although it may be true that "different alloys change during aging in a quite different manner as indicated by coersive force and no broad correlation is possible"—I feel that in alloys of the same type magnetic properties are a very sensitive and reliable criterion in studying changes due to aging. With a reasonable amount of care introduction of external stresses may be completely avoided.

In a paper presented a short time ago by T. D. Yensen and myself[8] a few

[8]T. D. Yensen and N. A. Ziegler, "Magnetic Aging of Iron Due to Oxygen," *Metals Technology*, June 1935, Technical Publication 624. American Institute of Mining and Metallurgical Engineers.

experiments describing the effect of dissolved oxygen on changes in magnetic properties of unalloyed iron are presented, and I am glad to notice that our results check with those now under discussion. In our curves (1, Fig. 8) time of aging remains constant, and aging temperatures increase with every consecutive step, while in the curves, Fig. 8 and 12, of the present paper aging temperature remains constant, and time of aging is increasing. Nevertheless a typical "aging" change in properties is observable in both cases.

It seems that a relatively small "aging" change indicated in the curve for oxygen-saturated electrolytic iron at 70 degrees Fahr. (20 degrees Cent.), lower block, Fig. 8 of the present paper, may be explained by the fact that this sample, previous to the aging treatment, was quenched from 1325 degrees Fahr. (720 degrees Cent.), which is too low for any appreciable amount of oxygen to go into solid solution.[6]

In our curves (1, Fig. 8) a considerable "aging" change in the sample quenched from the same temperature may be explained by the fact that magnetic properties are far more sensitive than hardness as indicated by the Rockwell test, and that small amounts of precipitates which may completely alter the former remain quite ineffective upon the latter.

Oral Discussion

DR. ANSON HAYES:[7] Had I nothing else to say I would feel that I should at least say a word in regard to the clear presentation and the great simplification that the authors of this paper have brought about. There are two topics on which I should like to remark. I do not disagree in any way with the statements which the authors have made. The first remark is in regard to the condition under which elongation at the yield point in the tensile stress strain diagram takes place. I believe that the statement as made by the authors probably is incomplete. The conditions under which elongation at the yield point and the consequent stretcher strain take place are not necessarily that the crystals of the deformed metal are weaker after deformation than the unstrained crystals. This is because there are two processes going on in the pulling of the tensile test piece, one of which is a reduction in area which, if there were no other changes taking place would be a weakening process. The other is a cold working process which usually has a hardening effect so that as long as the rate of weakening is greater in its total amount than the strengthening due to cold working, there will be elongation at the yield point and stretcher straining will result.

There is another approach to the support of the contention of the authors that oxygen is the major factor in strain aging. This resides in the fact that if one starts alloying varying amounts of the three strong deoxidizers, silicon, titanium, and aluminum, it is found at a certain alloyed silicon content, that it is possible to heat treat the material in such a manner as to make it essentially free from strain aging. Starting with smaller amounts of titanium and increasing them to certain limiting values, it is found that a similar behavior is obtained, except that the limiting amount of titanium that is neces-

[6] N. A. Ziegler, "Solubility of Oxygen in Solid Iron," TRANSACTIONS, American Society for Steel Treating, Vol. 20, 1932, No. 1, p. 73.

[7] Director, Research Laboratories, American Rolling Mill Co., Middletown, Ohio.

sary to make a stabilized material is considerably smaller than that of silicon. If the same series of experiments be conducted with aluminum, a still lower limiting alloyed amount of aluminum is found to make a stabilizable material. One property that is in common with these three elements is that they are strong deoxidizers, and in open-hearth steel when nitrogen is as small as it usually is, we feel that this evidence in connection with these strong deoxidizers is very greatly supporting the idea that oxygen is the important factor.

I notice that the authors have used after considerable consideration, the Rockwell hardness test, as a means of measuring the progress of both quench and strain aging. I would like to refer to a paper which was written by R. L. Kenyon and R. S. Burns, of our laboratory, presented before the A.S.T.M. (A.S.T.M., Vol. 34, Part II, 1934, p. 48-58). This test consists in determining the tensile strength of the material at 400 degrees Fahr. and again at room temperature, of course, using two different test bars of the same material. It is well known that with ordinary mild steel of the rimming variety, the increase in tensile strength at 400 degrees Fahr. over that of room temperature, may be as high as some 10,000 pounds per square inch. With the usual behavior of metals with variation in temperature, there is a decrease in tensile strength as the temperature is raised, and with materials that are most stable against strain aging, it is found that the tensile strength at 400 degrees Fahr. is as high as 10,000 pounds per square inch less than that at room temperature. Between the very marked increase in tensile strength that is obtained in those materials that are very subject to strain aging, and materials that are essentially stable against strain aging, there is a range of some 20,000 pounds per square inch in which to work and with which to measure tendency to strain aging. With such a tool as this, the effect of normalizing and the effect of a subcritical heat treatment are very easy to follow, and are pronounced in those grades of steel that involve carbon in the ranges usually used in automobile body sheets.

Dr S. L. Hoyt:[8] I should like to ask a question. To show what I have in mind I would like to divide the paper into four parts. 1A deals with the facts of quench aging; and 1B correlates them with the theory of precipitation hardening. This gives a rational picture of quench aging. 2A relates to facts of strain aging, but 2B seems to be missing from this paper and that is what my question relates to. What theory do the authors have which will account for why it is that oxygen has these effects? They are very definite and very pronounced effects of course, and it seems to me that it is about time "to explain" them better than has been done in the past. I take the liberty to propose this question to the authors because they have demonstrated in the past very great ingenuity in accounting for the data they have observed in the laboratory. I would say however, that I am using theory in a little different way than it was used by Dr. Arnold. It seems to me that what Arnold does is to set up more of a mnemonic system rather than a theory, and so, I would like to make that distinction in asking my question.

[8]Director of research, A. O. Smith Corp., Milwaukee.

Authors' Closure

The authors deeply appreciate the many valuable additions to the knowledge of aging in steel which have been brought out in the discussion of their paper; these discussions constitute a criticism which has the real merit implied by "criticism" in its best sense. To Messrs. Epstein, Ziegler, Hayes, Arnold and Hoyt the authors extend their sincere thanks for the interest in their report which is shown by the thoughtful remarks. This paper on aging is intended to set forth the simplest concept which can possibly account for the observations; it is to be expected that further adjustment of this basic explanation by additional factors or revisions will become necessary with continued increase in knowledge gained from experimental study.

With respect to the discussion of Dr. Anson Hayes there is no doubt that tensile testing, at 400 degrees Fahr. and at room temperature is a splendid way of measuring the susceptibility of different steels to aging. Only when hundreds of measurements must be taken to establish the characteristic trend or pattern of the aging reaction must one choose a simpler measurement which consumes little time. Hardness then recommends itself as an excellent compromise criterion of aging. The point raised by Dr. Hayes as to the underlying reason for abrupt yield and stretcher straining is worthy of careful consideration. We are in the habit of explaining maximum tensile strength by regarding it as the state of affairs at which reduction of effective cross section just becomes a more potent factor than the strengthening by cold work; it is of course possible that in the early stages of deformation also, reduction of area could be a more potent factor than strengthening by cold work. However, since the phenomenon of abrupt stretch is so rare it seems necessary to invoke other bases of explanation. In any event the constriction mentioned by Dr. Hayes must be taken into consideration even though it should be found insufficient to explain the whole of the phenomenon.

Dr. Ziegler's remarks are very helpful in assigning a more definite position to magnetic properties as a criterion of aging. It may be, however, that the changes in coercive force accompanying aging in supersaturated solid solutions are largely dependent upon balanced stresses of microscopic distribution which are set up by volume changes. Such stresses, if existent, would not be dissipated by any prior treatment or by an experimental technique, but would vary greatly depending upon the density of the precipitated phase.

It is of great interest also to note the suggestions of Mr. Epstein and his word of caution regarding the simplicity of the authors' concept of aging. The point is well made, and the authors are well aware of the solubility of nitrogen as found by one observer. Certainly the matter of supersaturation with respect to nitrogen must receive more study; all one can say is that the phenomena usually observed do not necessitate a nitride precipitation for their explanation, and that the pattern is not in agreement with what would be expected from nitrogen.

It has already become fairly evident to the authors that the phenomenon designated "caustic embrittlement" may, in all probability, be a complex one and they therefore point out merely that oxygen, or the strain-aging element, appears to be involved with that aspect of it which may be recognized by their mode of study.

With respect to the quench-aging of very low oxygen steel the authors must insist firmly that they have found quench-aging to occur extremely vigorously in steel which carries oxygen in far smaller quantities than any commercial metals,—even in the presence of half of one per cent dissolved aluminum. As to results in disagreement with this observation it should be remembered that quench-aging is often scarcely discernible in steels carrying over 0.12 per cent carbon and feeble even at lower carbon contents.

This calls up the question of the simultaneous occurrence of quench-aging and strain-aging. The authors surely intended to indicate, by showing both the charts of Fig. 11, that it is important to remember that actually both reactions may occur together; what the authors regard as new is the scheme of isolating each for independent *experimental* study by one means or another. This is perhaps a matter of some significance as it determines the viewpoint from which the paper is approached.

The contribution of Dr. Arnold is a valuable statement of some of the speculative aspects of the theories of precipitation which should be considered in connection with any study of age-hardening. Beyond question the loss of ductility or embrittlement is a significant manifestation of precipitation or pre-precipitation phenomena; however, once a precipitation reaction is perceived and recognized, another manifestation may well be used as a means of following its rates and inherent characteristics, especially after one or more correlations have been made with ductility tests. It is to be hoped that Dr. Arnold may find occasion to prepare a paper based upon the views briefly expressed here amplified by suitable experimental data.

Regardless of consequence, the authors cannot wholly resist the temptation to accept the challenge from Dr. Hoyt to offer some sort of explanation of the unique characteristics of strain-aging,—in short, something to fill in the missing "Section 2B." Probably no one could make a better job of "Section 2B" than Dr. Hoyt himself, but as he has offered the authors the opportunity, they have no choice but to try what may be done.

First of all the authors decline to attempt any answer to a question beginning with "why," because any answer automatically asks another question, "why." The best they can offer by way of explanation will be a possible "how," not too violently incongruous with the mass of observations already made.

The authors regard that the accumulated knowledge regarding precipitation from supersaturated solid solutions favors, for the general case, the following views:

1. That the major portion of the effect upon mechanical properties results from the earliest stages of the rejection of the excess solute; one might say from the first molecular rejections, i.e, "knots," or perhaps single molecules.

2. That in many cases the numerical maximum of these really effective pre-precipitation loci is reached only after a fair number of actual crystallites at other loci have formed. These actual crystallites composed of several molecules are comparatively of little consequence in hardening effect although often they appear to be the cause of marked black-etching phenomena.

3. That the hardening characteristics attending the release of super-

saturation relates to a very complicated and little understood function having to do with chemical activity of compound formation and the characteristic of the solvent crystal and the compound crystal. It probably has relatively little to do with diffusivity. A compound having a high heat of formation may form with reluctance in a crystal grain and require a fairly high aging temperature. It may form more rapidly in an amorphous or badly crystallized region such as a grain boundary or slip band.

4. That subsequent softening by over-aging relates mainly to diffusivity. If the solute element has relatively low diffusivity, then high temperatures are required for over-aging.

5. A compound of weak combination activity and high diffusivity may induce over-aging promptly at the lowest age-hardening temperatures.

6. A compound of high rate of combination and low diffusivity may produce a system in which over-aging occurs promptly only at temperatures far above rapid age-hardening temperatures. This must be the case in strain-aging.

7. The element responsible for strain-aging, believed to be oxygen, has high combining activity with iron in only the disturbed crystal at grain boundaries and slip planes, and results in age-hardening at room temperature in cold-worked metal. Only at higher temperatures is any appreciable hardening observed in annealed supersaturated grains. This element must have low diffusivity because of the reluctance to over-age. Oxygen is known to have low diffusivity in iron.

Now this explanation, like most explanations, is little more than a restatement of the observations and introduces only the idea that the iron-oxygen compound, for some reason, is reluctant to form even as molecules in the crystal of iron but does so well enough in disturbed metal. The other idea, that the diffusivity is important to over-aging is equally well corroborated by other experience. Corson found age-hardening systems in which the supersaturation could not be preserved at all at room temperature, but yet over-aging did not occur at once even at quite elevated temperatures. The chromium-rich carbide of high chromium steels is reluctant to form within any grain but forms well enough by aging at moderate temperatures either at grain boundaries or on slip planes.

Thus the authors have only been able to "explain" the observed peculiarities of strain-aging by assigning certain definite properties—not too improbable—to the iron-oxygen compound formation. Whether or not this is correct can only be shown by some independent studies, and even the nature of such studies remains unknown so far as the authors are aware.

The authors wish to add an acknowledgment of a communication from Joseph Winlock of the Edward G. Budd Manufacturing Company, who calls attention to an observation of marked, sudden yield having been made upon nonferrous metals, copper and brass. Dr. P. Schoenmaker* of Holland made observations of this phenomenon at very low temperature, −80 degrees Cent., and also in some cases at −30 degrees Cent. This is believed to be the first observation of this sort in metals other than iron.

*First Communications of the New International Association for the Testing of Materials, Group A, p. 237-251, Zurich, 1930.

THE ORIENTATION OF CRYSTALS IN SILICON IRON

By Richard M. Bozorth

Abstract

X-ray examination of silicon iron prepared by N. P. Goss shows that the component crystals are oriented so that a [0 0 1] direction is parallel to the direction of rolling and a (1 1 0) plane lies in the rolling plane. This is contrary to the result reported by Goss. The differences in the magnetic properties in different directions in the sheet, are explained in terms of the properties of the single crystals.

IN a recent paper, Goss[1] described the preparation of silicon iron having some interesting magnetic properties. In a sample of this material kindly supplied the author by Mr. Goss, the maximum permeability measured in the direction of rolling is more than 20,000, and the permeability at B = 16,000 is about 2000. When measured in a direction perpendicular to the rolling direction the permeabilities are not so high; in some other directions the permeabilities are still lower. This shows that the material is magnetically anisotropic; and its properties resemble in a striking way the properties of a single crystal of iron.

After emphasizing these facts, Goss considered the possibility that the crystals in the final product are oriented in a special way by the rolling. He concluded from X-ray diffraction photographs of several specimens that the crystals were oriented at random. This conclusion, as Goss points out, necessitates a revision of present-day theories regarding the ferromagnetic properties of single crystals and fine-grained aggregates.

The writer's interest in theories of magnetization led him to repeat the X-ray tests with material supplied by Mr. Goss. It has been found that the crystals are not arranged at random, but in such a way that one of the six directions of easy magnetization in each crystal

[1] N. P. Goss, "New Development in Electrical Strip Steels Characterized by Fine Grain Structure Approaching the Properties of a Single Crystal," Transactions, American Society for Metals, Vol. 23, June 1935, p. 511. See also the discussion by N. P. Goss of W. E. Ruder's paper entitled "The Influence of Grain-Size on Magnetic Properties," Transactions, American Society for Metals, Vol. 22, 1934, p. 1133.

A paper by Richard M. Bozorth, Bell Telephone Laboratories, 463 West St., New York City. Manuscript received May 4, 1935.

lies approximately parallel to the direction of rolling, in which direction the strip is observed to have its unusual magnetic properties. It seems fair to conclude that present-day theories of magnetic single crystals need no radical revision. This brief paper, offering as it does a theory for the observed magnetic effects (which was not regarded as tenable by Goss), relates in no way to the practical value of his product.

The X-Ray Data

From strips 0.011 by 1.0 inch containing 3.5 per cent silicon, in the final annealed condition for which the permeabilities are high, several two-inch lengths were cut and etched rapidly in aqua regia to a thickness of 0.005 inch. One of these was so mounted in a beam of X-rays from a molybdenum target that it could be rotated around an axis lying in the plane of the sample perpendicular to the X-ray beam. The axis of rotation was either the direction of rolling (R.D.) or the cross direction (C.D.). The rotation was usually from grazing angle 0 to 25 degrees from that position, and was at approximately constant angular velocity. A photographic plate was placed perpendicular to the beam, 10 centimeters (3.9 inches) beyond the axis of rotation.

The photographs showed reflections due to the characteristic Mo Kα X-rays of wavelength 0.710 A. Since the grain-size of the specimen was not very small in comparison with the cross section of the X-ray beam, the number of crystals reflecting was rather small, and the reflections recorded on the photographic plate consisted of short straight lines about as long as the central image and parallel to it. For this reason it was difficult to estimate the relative intensities in various portions of the Debye-Scherrer circles. Using the data from several photographs, however, arcs could be drawn which were estimated to contain three-quarters or more of the reflections. These are reproduced in Fig. 1, where (a) refers to the photograph taken with the axis of rotation parallel to the cross direction as indicated. Fig. 1 (b) shows the corresponding arcs when the specimen is rotated around the rolling direction.

The crowding together of the reflections shows definitely that there is a special orientation of the crystals. In order to describe this orientation with reference to the crystal axis, a number of calculations were made. Various orientations were assumed for a single crystal placed so that simply indexed crystallographic directions coin-

cided with the rolling direction, the cross direction and the normal to the rolling plane. Calculation then determined the positions of the reflected beams from the (1 1 0), (2 0 0), (2 1 1) and (2 2 0) planes of this crystal when oriented in the specimen in each of the

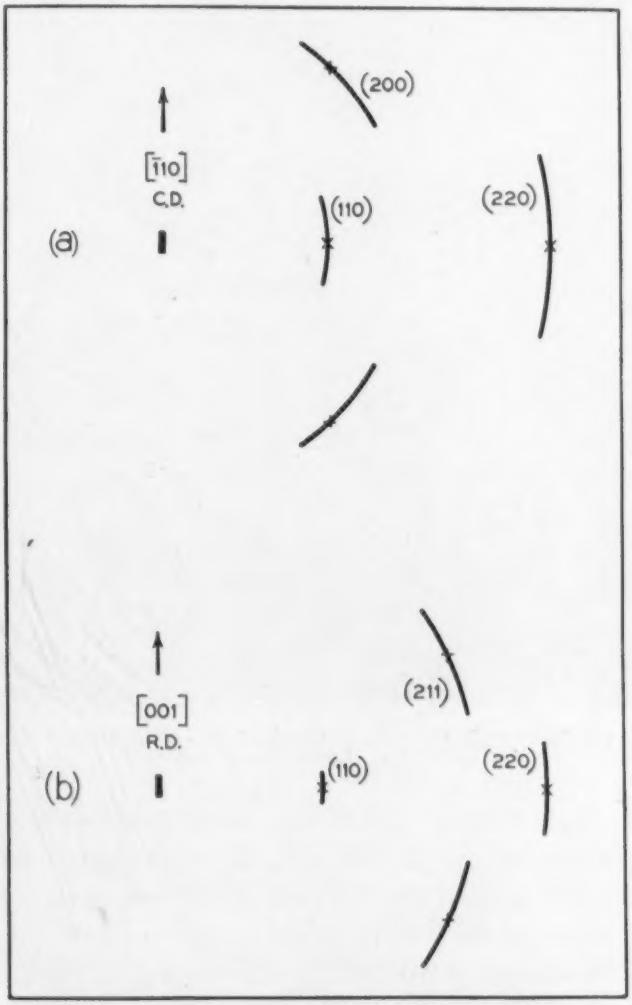


Fig. 1—Arcs Represent X-ray Reflections when Specimen is Rotated (a) Around Cross-Direction, (b) Around Rolling-Direction. Notice that (2 1 1) Reflections Are Missing in (a) and (2 0 0) Reflections in (b). Crosses represent calculated Positions of Reflections for perfect alignment of crystals.

assumed ways and rotated with it. It was assumed that for reflections to appear, the incident and reflected beams must enter and leave the same surface of the specimen. The crosses of Fig. 1 show all of the positions of the reflections so calculated for one assumed orien-

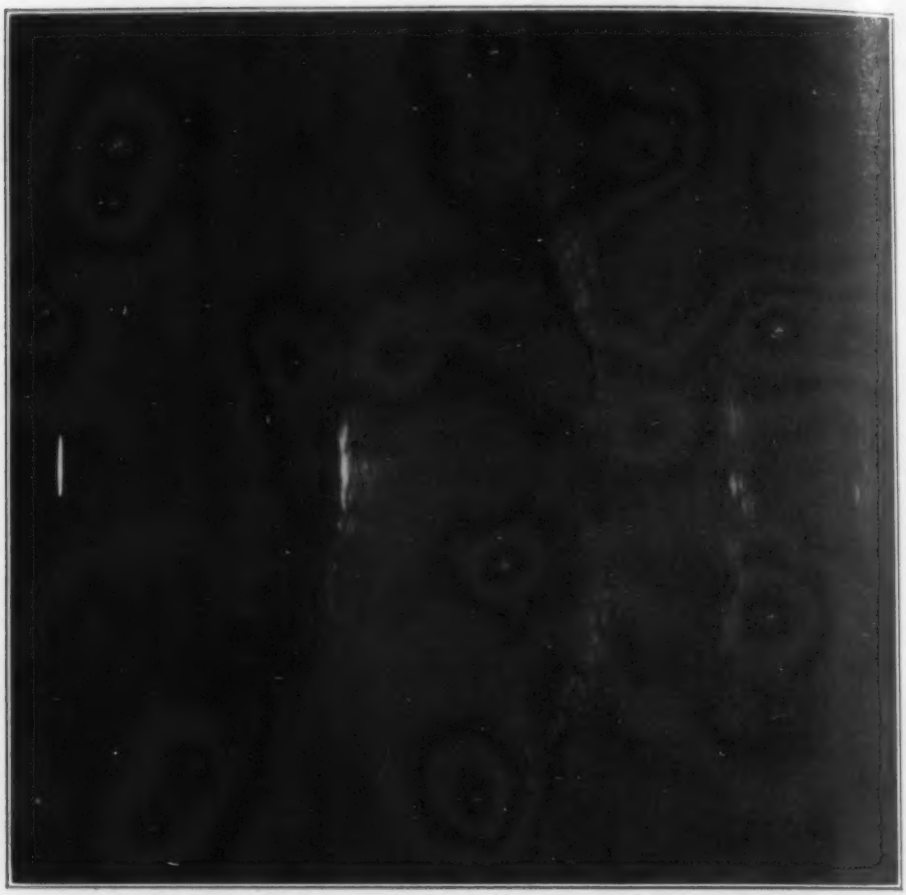


Fig. 2—X-ray Photograph (retouched) Obtained When Specimen is Rotated Around Rolling Direction. Notice that (2 0 0) Reflections Are Absent.

tation of the single crystal. Since this orientation is the only one for which the crosses all lie on the arcs, it is concluded that it is the actual mean orientation of the crystals in the specimen. It is:[2]

(1 1 0) plane in the rolling plane,

[0 0 1] direction parallel to the direction of rolling,

[1 1 0] direction parallel to the cross direction.

The deviation of the crystals from the average orientation can be estimated from the lengths of the arcs. A comparison of the lengths of the arcs for the (2 2 0) reflections in (a) and (b) of Fig. 1 illustrates this point. As drawn, the lengths of the arcs indicate that the normal to the (1 1 0) planes, instead of being exactly normal

[2]This orientation is not the same as any of the three found in hard rolled or recrystallized iron by G. Kurdjumow and G. Sachs, *Zeit. f. Physik*, Vol. 62, 1930, p. 592-9. It is one of those recently determined for silicon iron by K. J. Sixtus, *Physics*, Vol. 6, 1935, p. 105-11, using Tammann's optical method. The latter paper was published after the completion of the work described in this note.

to the rolling plane of the specimen, varies as much as 8 degrees toward the rolling direction and 15 degrees toward the cross direction. It is estimated that from three-quarters to nine-tenths of the crystals lie within these extreme variations.

Fig. 2 is a reproduction (retouched) of one of the photographs taken by oscillation about the cross direction, corresponding to Fig. 1 (a). The photographs reproduced in Goss' paper are taken without rotation of the sample with respect to the X-ray beam. The reflections do not fall into rings, so that they are obviously due to general radiation and do not show whether special orientation is present or not.

Relation of the Results to Magnetism

The results of the X-ray tests show that the [0 0 1] direction lies parallel to the rolling direction, which is also the direction in which the magnetic properties were determined. The results of magnetic investigations of iron crystals show also that directions of form <0 0 1> are those in which the crystals are most easily magnetized. It is to be concluded that the high permeability of Goss' silicon iron as compared with other silicon iron, and especially the high permeability in one direction, is due to the favorable orientation of the crystals composing it.

TECHNICAL PROGRAM AND REPORTS OF OFFICERS AMERICAN SOCIETY FOR METALS—17th CONVENTION CHICAGO, SEPTEMBER 30-OCTOBER 4, 1935

FOR purposes of record and for the benefit of members who were not in attendance at the Seventeenth Annual Convention of the Society, the Technical Papers Program and Reports of Officers presented at the annual meeting are herewith published in full.

MONDAY, SEPTEMBER 30

Morning Session—Palmer House Ball Room—10:00 A. M.

Joint Chairmen—H. A. Anderson and H. J. Stein

Metallographic Session

On the Preparation of Iron and Steel Specimens for Microscopic Investigations, by F. F. Lucas, Bell Telephone Labs., New York.

Oxalic Acid as an Electrolytic Etching Reagent for Stainless Steels, by G. A. Ellinger, National Bureau of Standards, Washington, D. C.

On Naming the Aggregate Constituents in Steel, by J. R. Vilella, G. E. Guellich, U. S. Steel Corp., Kearny, N. J., and E. C. Bain, U. S. Steel Corp., New York City.

Afternoon Session—International Amphitheatre—2:00 P. M.

Joint Chairmen—Dr. John Johnston and L. A. Lanning

Research Session

Arc Welding of High Carbon and Alloy Steels, by T. N. Armstrong, Norfolk Navy Yard, Portsmouth, Va.

A Dilatometric Study of the Alpha-Gamma Transformation in High Purity Iron, by C. Wells, R. A. Ackley and R. F. Mehl, Carnegie Institute of Technology, Pittsburgh.

Some Transient Phase Changes During the Graphitizing Reaction, by H. A. Schwartz, H. H. Johnson and C. H. Junge, National Malleable and Steel Casting Co., Cleveland.

International Amphitheatre—4:30 and 7:30 P. M.

Educational Lectures

Heat Treatment of Steel, by Dr. M. A. Grossmann, Illinois Steel Co., Chicago.

Spectrographic Analysis, by Dr. E. J. Martin, Research Division, General Motors Corp., Detroit.

TUESDAY, OCTOBER 1

Morning Session—Palmer House Ball Room—10:00 A. M.

Joint Chairmen—A. B. Kinzel and J. F. Wyzalek

General Session

Chromium Steels of High Nitrogen Content, by Russell Franks, Union Carbide & Carbon Res. Labs., Niagara Falls, N. Y.

Correlation of Failures from Embrittlement of 4 to 6% Chromium Steel with the Notched Bar Impact Test, by H. M. Wilten, The Texas Co., Port Arthur, Texas.

Factors Influencing the Nature of the Cutting Speed-Tool Life Curves, by O. W. Boston, W. W. Gilbert and C. E. Kraus, University of Michigan.

Morning Simultaneous Session—Palmer House—Parlor 10—10:00 A. M.

Joint Chairmen—J. P. Gill and E. F. Ross

General Session

High Temperature Properties of Nickel-Cobalt-Iron Base Age-Hardening Alloys, by C. R. Austin, Penn State College, State College, Pa.

Observations on the Oxidation of Steel, by M. Baeyertz, Illinois Steel Co., Chicago.

Effect of Grain-Size Upon Some Physical Properties of Medium Carbon Steels, by F. G. Sefing and K. J. Trigger, Michigan State College, Lansing, Michigan.

Afternoon Session—International Amphitheatre—2:00 P. M.

Joint Chairmen—H. M. Boylston and O. V. Greene

High Temperature Session

Physical Properties of Metals as Affected by Ammonia Synthesis, by H. L. Maxwell, E. I. duPont deNemours & Co., Wilmington, Del.

Influence of Carbon Content on the High Temperature Properties of Steels, by A. E. White, C. L. Clark, University of Michigan, and R. L. Wilson, Timken Steel & Tube Co., Canton, O.

A New Heat Resistant Alloy, by S. L. Hoyt and M. A. Scheil, A. O. Smith Corp., Milwaukee, Wis.

International Amphitheatre—4:30 and 7:30 P. M.

Educational Lectures

Heat Treatment of Steel, by Dr. M. A. Grossmann, Illinois Steel Co., Chicago.

Spectrographic Analysis, by Dr. E. J. Martin, Research Div., General Motors Corp., Detroit.

WEDNESDAY, OCTOBER 2

Morning Session—Palmer House Ball Room—9:30 A. M.

ANNUAL MEETING OF THE A.S.M.

1935 Edward De Mille Campbell Memorial Lecture presented by H. W. McQuaid, Republic Steel Corp., Massillon, Ohio

Chairman—Professor Bradley Stoughton

Afternoon Session—International Amphitheatre—2:00 P. M.

Joint Chairmen—H. J. French and K. R. Van Horn

Grain-Size Session

Effect of Carbon, Oxygen and Grain-Size on the Magnetic Properties of Iron-Silicon Alloys, by T. D. Yensen, Westinghouse Electric & Mfg. Co., E. Pittsburgh, Pa., and N. A. Ziegler, West Penn Electric Co., Pittsburgh, Pa.

Grain-Size and Its Influence on Surface Decarburization of Steel, by D. H. Rowland and Clair Upthegrove, University of Michigan, Ann Arbor, Mich.
Austenitic Grain-Size in Cast Iron, by D. W. Murphy, and W. P. Wood, University of Michigan, Ann Arbor, Mich.

International Amphitheatre—4:30 P. M.

Educational Lecture

Heat Treatment of Steel, by Dr. M. A. Grossmann, Illinois Steel Co., Chicago.
Spectrographic Analysis, by Dr. E. J. Martin, Research Div., General Motors Corp., Detroit.

THURSDAY, OCTOBER 3

Morning Session—Palmer House Ball Room—10:00 A. M.

Joint Chairmen—O. E. Harder and A. E. White

Research Session

Notes on the Solidus Temperature in the Systems Iron-Tungsten and Iron-Molybdenum, by W. P. Sykes, General Electric Co., Cleveland.
The Influence of Deoxidation on the Aging of Mild Steels, by B. N. Daniloff, R. F. Mehl, Carnegie Institute of Technology, Pittsburgh, and C. H. Herty, Jr., Bethlehem Steel Co., Bethlehem, Pa.
The Aging of Steel, by E. S. Davenport, U. S. Steel Corp., Kearny, N. J., and E. C. Bain, U. S. Steel Corp., New York City.

Afternoon Session—International Amphitheatre—2:00 P. M.

Joint Chairmen—W. E. Harvey and Jerome Strauss

Research Session

Endurance of Case Hardened Gears, by O. W. McMullan, International Nickel Co., Bayonne, N. J.
Pickle Pitting by Electrolytic Potentials as Affected by Scaling Temperatures, by C. H. McCollam, and D. L. Warrick, Timken Steel & Tube Co., Canton, Ohio.
Damping Capacity, A Factor in Fatigue, by G. R. Brophy, General Electric Co., Schenectady, N. Y.

International Amphitheatre—4:30 and 7:30 P. M.

Educational Lectures

Heat Treatment of Steel, by Dr. M. A. Grossmann, Illinois Steel Co., Chicago.

7:00 P. M.—Palmer House Ball Room

ANNUAL BANQUET OF THE A.S.M.

FRIDAY, OCTOBER 4

Morning Session—Palmer House Ball Room—10:00 A. M.

Joint Chairmen—H. L. Day and Howard Stagg

Tool Steel Session

Hardening Characteristics of One Per Cent Carbon Tool Steels, by T. G. Digges and Louis Jordan, National Bureau of Standards, Washington, D. C.

Interpretation of Torsion Impact Properties of Carbon Tool Steel, by G. V. Luerssen and O. V. Greene, Carpenter Steel Co., Reading, Pa.

Contributory Effects of Furnace Atmospheres on the Grain-Size of Molybdenum High Speed Steel, by Arthur Phillips and M. J. Weldon, Yale University, New Haven, Conn.

Afternoon Session—International Amphitheatre—2:00 P. M.

Joint Chairmen—C. H. Herty, Jr., and N. I. Stotz

Steel Making Session

Open-Hearth Temperature Control, by Earnshaw Cook, American Brake Shoe & Foundry Co., Chicago Heights, Ill.

The Effect of Deoxidation on the Rate of Formation of Ferrite in Commercial Steels, by D. L. McBride, Carnegie Institute of Technology, Pittsburgh, C. H. Herty, Jr., Bethlehem Steel Co., Bethlehem, Pa., and R. F. Mehl, Carnegie Institute of Technology, Pittsburgh, Pa.

Equilibrium in the Reaction of Hydrogen with Ferrous Oxide in Liquid Iron at 1600 Degrees Cent., by John Chipman, American Rolling Mill Co., Middletown, Ohio, and M. Fontana, E. I. duPont deNemours & Co., Wilmington, Delaware.

International Amphitheatre—4:30 P. M.

Educational Lecture

Heat Treatment of Steel, by Dr. M. A. Grossmann, Illinois Steel Co., Chicago, Illinois.

ANNUAL ADDRESS OF THE PRESIDENT

Seventeenth Annual Convention, Chicago, October 2, 1935

B. F. SHEPHERD, *President*

WE have just passed through a period of severe industrial disturbance. Conditions at the present time throughout the country indicate definitely that the so-called depression is over. The country has made marvelous progress during the past year. Your Society has made even more remarkable progress.

The depression was a challenge to initiative, courage and ability. Your country responded to this challenge. Your Society, likewise, responded to this challenge with even greater energy. At the first opportunity the National organization and individual Chapters took it upon themselves to renew the dissemination of metallurgical information, so that their members could more efficiently participate in accelerating the industrial recovery and be better prepared to take their part in this work.

The object of this report, however, is not to discuss economics

but to tell you something of the status of your Society as of the present date, and the work which has been done during the past year.

An enviable record has been made. A fitting climax is this Seventeenth National Metal Congress and Exposition, now in progress.

This Exposition and Congress should illustrate to each and every one of you the relative importance of your particular field of endeavor. Metallurgy is not by any means a minor factor in our industrial life. More and more our designing engineers and the general public realize that our progress is a function of not how fast can we make it, but how long will it stand up, and how much better can it be made—machine tools, motor cars, railroads, rock drills, aeroplanes and all mechanical equipment must not only have a low initial cost, but each and every part must also withstand the service requirements to the "nth degree." We must realize we are only on the threshold of developments to come. As members of your Society, you have a tremendous responsibility. You must be ready and prepared to carry on this job.

I have been particularly fortunate in being able to visit 60 per cent of our forty chapters. It is not generally realized that there is a considerable demand upon the time of your President, in addition to his executive and other duties in visiting the chapters. Chapters can only be visited on five days of the week. Simple arithmetic will indicate that it would take eight consecutive weeks to visit each and every Chapter, provided geographical location and dates of meetings were not a factor. Therefore Chapters should not feel slighted if they do not receive a personal visit from the President. Such an attitude might react some day to prevent a most desirable man from becoming our leader.

It is with distinct pleasure and recognition of work well done that your president has been able to observe the splendid work that has been accomplished in the chapters of the Society during the period of his administration.

The caliber of the chapter meetings, together with the encouraging and splendid attendance at the sectional meetings and the outstanding attendance at this annual meeting, indicates a great interest in the work and progress of the Society.

The financial report that you are to hear later, presented by Treasurer Gathmann, and the splendid standing of the Society with reference to its membership, are a source of satisfaction and pride to the Board of Trustees.

During the past year your Board of Trustees has held five meetings. The first were in Cleveland on November 9th and 10th, 1934, with subsequent meetings on June 14th, 1935, and September 30, 1935, in Chicago, and October 1st, 1935, in Chicago.

There has been excellent co-operation during this period on the part of the members of the Board of Trustees, and I speak for them in expressing their sincere appreciation for the work of the various national committees of the Society.

They are greatly appreciative of the conscientious, sincere and worth while efforts and contributions of the committees to the successful work the Society has accomplished.

The Trustees desire to express their appreciation to Dr. Marcus A. Grossmann, who has so splendidly presented a series of lectures on the "Principles of Heat Treatment" during the present convention.

At the same time Dr. E. J. Martin is also a recipient of our thanks for his series of enlightening lectures on the subject of "Spectrographic Analysis." I wish to personally express my appreciation of the assistance rendered me by our "one and only" Secretary W. H. Eisenman.

It has been a great pleasure for me to contribute my efforts in behalf to the Society, of which I have been a member so long.

Our Society has suffered an irreparable loss during the past year. Our beloved, honorary member, Dr. John Alexander Mathews, is no longer with us. I think it entirely fitting and proper if at this time in memory of this great scientist, the friend and helpmate of so many of us, that we rise for a moment to honor his memory.

We are deeply appreciative of the co-operation of the American Welding Society, The Institute of Metals Division and the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers, and the Wire Association, in helping to make this our Seventeenth National Metal Congress a success, and I welcome them to each and every one of our activities. These societies and their committees have supplemented the technical program to such a degree that this Congress is an evidence of the greatest concentration of metallurgical effort of all time.

President's Medal

The President's Medal was presented to Past-President W. B.

Coleman at the annual banquet during the convention in 1934. The medal was indicative, in this case, of a definite and tangible memento of appreciation to Mr. Coleman for his five years of official service to the Society and his administration as president.

Howe Medal Award

The Henry Marion Howe Medal awarded annually for the paper of highest merit published in TRANSACTIONS during the year, was awarded for the year 1934 to Dr. John Chipman, who was Research Engineer, Department of Engineering Research, University of Michigan, and is now Associate Director of the Research Laboratories, American Rolling Mill Company, Middletown, Ohio. Dr. Chipman's paper was entitled, *"Application of Thermo-Dynamics to the Deoxidation of Liquid Steel."*

For the year 1935 the committee of award has unanimously selected Dr. T. D. Yensen of the Westinghouse Electric and Manufacturing Co. and Mr. N. A. Ziegler of the West Penn Electric Co. for their paper entitled, *"Magnetic Properties of Iron as Affected by Carbon, Oxygen and Grain-Size,"* published in TRANSACTIONS, June, 1935.

Campbell Lecture

The Campbell Memorial Lecture, established in 1925, by the Board of Trustees and honoring the memory of Edward DeMille Campbell of the University of Michigan, was presented in 1934 at the convention in New York by Dr. V. N. Krivobok, professor of metallurgy, Carnegie Institute of Technology, Pittsburgh, and associate director of research, Allegheny Steel Co., Brackenridge, Pa. The lecture was entitled *"Alloys of Iron and Chromium"* and was published in full in the March 1935 issue of TRANSACTIONS.

Albert Sauveur Achievement Award

The Albert Sauveur Achievement Award was established by the Board of Trustees in 1934. Dr. Sauveur, in whose honor the award was established, was made the first recipient at the annual banquet in New York. The award rests entirely in the hands of the past presidents of the Society, who constitute the Albert Sauveur Award Committee. This year I am pleased to report they have, after mature deliberation and consideration, selected one of America's

most distinguished and outstanding metallurgists, Dr. Zay Jeffries, to receive the award for 1935. The presentation will take place at the annual banquet tomorrow evening.

President's Bell

At the close of the administration of R. M. Bird in 1926, he established an award to be presented annually by the president to be known as the President's Bell, which would be awarded in recognition of the oustanding activities of the chapter as well as its contribution to the success of the Society.

During the past years it has been awarded to the following chapters:

1926—Lehigh Valley
1927—Golden Gate
1928—Philadelphia
1929—Los Angeles
1930—New Jersey
1931—Hartford
1932—Montreal
1933—Cleveland
1934—Cleveland

The responsibility falls upon me now to make a selection for the past year, and I admit that it is probably one of the most difficult undertakings that has been presented during my administration.

When one realizes the splendid work all of the chapters have done during the past year, as well as the actual growth of the Society, it is indeed a most perplexing situation.

However, it is necessary to make a decision, and I have selected a chapter which has never before been honored by this award, but which during the past year has increased its prestige in one of our large metal-working centers, and has been outstanding in the number, variety and attendance at its educational courses.

Their interest in the Society has been so great that the chapter now has the largest membership in the Society, and at the same time the largest membership ever held by a chapter of the A.S.M.

If Chairman Knowlton of the Chicago chapter will please come forward, it will afford me great pleasure to present to him the President's Bell. (Chairman Knowlton accepted the Bell and paid a compliment to the splendid work of preceding chapter chairman, Harvey A. Anderson.)

I am indeed grateful to the members of the Society for the honor and recognition that they have deemed proper to afford me. I have accepted the responsibilities of offices in the Society which I

have been called upon to fill, and have endeavored to discharge my obligations with a true regard for the confidence placed in me.

As my term as president comes to an end, I feel a degree of relief at the lifting of the load of responsibility, but I know there will always be in my mind a most pleasant recollection of my association on the board and a constant thought into the future for the welfare and success of the A.S.M.

REPORT OF THE TREASURER

October 2, 1935

EMIL GATHMANN, *Treasurer*

The unaudited balance sheet of the Society as of the close of business August 31, 1935, is as follows:

ASSETS				
Cash			$ 40,109.13	
Securities (at cost) Less Reserve, $30,000.00, and accrual			104,771.23	
Receivables less reserve			7,506.59	
Accounts with restricted banks			3,707.30	
Inventory			20,150.51	
Advances (for exposition, employees, chapters, post office, etc.)			8,091.62	
Office furniture and fixtures			3,780.00	
Prepaid expense (insurance, Metal Progress)			626.80	
1934 convention prepaid expense			18,595.06	
TOTAL ASSETS				$207,338.24
LIABILITIES				
Accounts payable (chapter refunds)			$ 392.27	
Reserves			45,000.00	
1934 convention advance receipts			40,190.00	
Surplus, Jan. 1, 1935		$144,403.77		
Plus net gain to Aug. 31		5,836.18		
Plus net gain 1934 convention		5,612.19		
Plus miscellaneous adjustments		16.63		
		$155,868.47		
Less reserve set up	$ 33,000.00			
Less interest defaulted	1,112.50	34,112.50	121,755.97	
				$207,338.24

Our cash is approximately $17,000.00 more than a year ago, receivables the same, and inventory about $2,000.00 more, while we still have $3,700.00 with restricted banks. The market value of our securities has continued to show improvement, the present value of $109,805.00 showing a gain of $6,500.00, or approximately 6 plus per cent over the value of $103,295.00 reported last year.

Reserves have been set up of $30,000.00 to offset the difference between the cost value of securities as shown on the books and the

present market value; also, a reserve of $3,000.00 to cover depreciation in value of bound volumes carried on our inventory.

Careful examination and consideration of our holdings by your treasurer and the board of trustees has not shown where our investments could be materially improved without considerable sacrifice and our investment account shows the same holding as of July 1, 1934 ($54,000.00 being in Government bonds). Our present holdings show $35,000.00 invested in utility bonds, $20,000.00 in railroad securities, $20,000.00 in industrial securities, in addition to our Government bond holding. The intention is to replace any maturing securities with Government bonds or bonds backed by the Government.

We have not found it necessary to dispose of any securities to meet operating expenses during the past year, but have on the other hand been able again to operate the Society within its income and to add to our surplus $11,464.70.

As the fiscal year of the Society now starts with September 1, the books of the Society have been audited as of August 31, 1935, and show the results as above.

Our income and expense statement as of August 31, 1935, covering the period from September 1, 1934, is as follows:

Income	$127,143.76	
Expense	121,307.58	
Excess income over expense		$ 5,836.18
1934 convention income	$ 45,409.54	
1934 convention expense	39,797.35	5,612.19
Total excess of income over expense		$ 11,464.70

Gross income from METAL PROGRESS has increased approximately 40 per cent this year over a like period in 1934, but expense due to increased circulation and editorial contents have increased in approximately the same proportion and no net financial profit was obtained.

The sales of books published, including Metals Handbook have been good and have helped materially in enabling the Society to show an addition to surplus.

The increase in membership dues receipts, however, has been largely responsible for the fine position the Society shows in its financial statement ending August 31, 1935. There has been a steady increase in the membership, the gross receipts being approximately $24,000.00 more than last year, which of course, was only an eight-month period.

CONDENSED AUDITED BALANCE SHEET

AMERICAN SOCIETY *for* METALS

As of August 31, 1935

ASSETS		
CASH		
On Hand	$ 400.00	
On Deposit	39,709.13	$ 40,109.13
SECURITIES		
U. S. Government Bonds	$ 54,250.65	
Other bonds	79,037.50	
Accrued interest	1,483.08	
	$134,771.23	
Less—Reserve	30,000.00	104,771.23
Accounts Receivable	$ 8,445.48	
Less—Reserve	928.18	7,517.30
Inventory		20,150.51
OTHER ASSETS		
Travel Advances, Employees' Accounts, etc.	$ 8,209.26	
Deposits in Restricted Banks	3,666.43	11,875.69
Office Furniture and Fixtures less Depreciation		3,780.00
Prepaid Expense (Convention, Metal Progress, Insurance)		21,946.72
		$210,150.58
LIABILITIES		
Accounts Payable		$ 3,204.61
Reserves		45,000.00
Advance 1935 convention receipts		40,190.00
Surplus		121,755.97
		$210,150.58

The above from Balance Sheet prepared by Ernst & Ernst, Certified Public Accountants.

INCOME AND EXPENSE

AMERICAN SOCIETY *for* METALS

For the year ended August 31, 1935

INCOME			
"METAL PROGRESS"—MONTHLY PUBLICATION			
Advertising		$56,685.50	
Subscriptions		1,966.12	
Reprints		1,423.78	
Sales		102.30	$60,177.70
MEMBERSHIPS			
Membership dues	$73,330.83		
Sustaining exhibitors' dues	4,075.00	$77,405.83	
Less: Apportionment of dues to chapters		29,355.29	48,050.54
1934 Convention—New York			45,409.54
Books published and purchased for resale			7,559.93
Interest earned			4,898.02
"Transactions"—bound copies, subscriptions, etc.			4,393.42
Discount earned			960.80
Chapter technical service			495.99
Miscellaneous			406.71
General reprints			352.59
"The Review"—advertising and subscriptions			82.30
TOTAL INCOME			$172,787.54

EXPENSE AS SHOWN BY EXHIBIT			
"Metal Progress"—monthly publication	$60,647.74		
1934 Convention—New York	39,797.35		
Books published and purchased for resale	8,279.59		
"Transactions"—bound copies, subscriptions, etc.	15,427.22		
General expense	7,696.08		
Chapters	3,093.32		
"The Review"	2,537.12		
Secretary's Office	13,976.10		
Accounting department	4,222.31		
Directors' expense	2,484.03		
National committees	1,091.92		
President's expense	724.36	$159,977.14	
Lectures, medals, etc.		466.27	
General index		284.63	
Books for library		238.96	
Reprints purchased for resale		137.93	
TOTAL EXPENSE			$161,104.93
NET PROFIT			$ 11,682.61

The above from Income and Expense sheet prepared by Ernst & Ernst, Certified Public Accountants.

It is interesting to note that in addition to the assets of the National Society of $207,338.24, the total cash assets of our chapters amounted to approximately $52,000.00 at the date of this report, which is an increase of about $5,000.00 over the report of last year.

It has been a real pleasure to serve our Society and your Treasurer's duties have been rendered most agreeable due to actual cooperation of the Trustees, Presidents Phillips and Shepherd, and our Secretary, Mr. Eisenman, during the past two years.

ANNUAL REPORT OF THE SECRETARY

October 2, 1935

W. H. EISENMAN, *Secretary*

The American Society for Metals, on October 1, 1935, had a total membership of 6880. Of this number 6130 or 89 per cent were the member classification, 446 or 6.5 per cent were of the sustaining classification, 282 or 4 per cent were of the junior classification, with 22 honorary members.

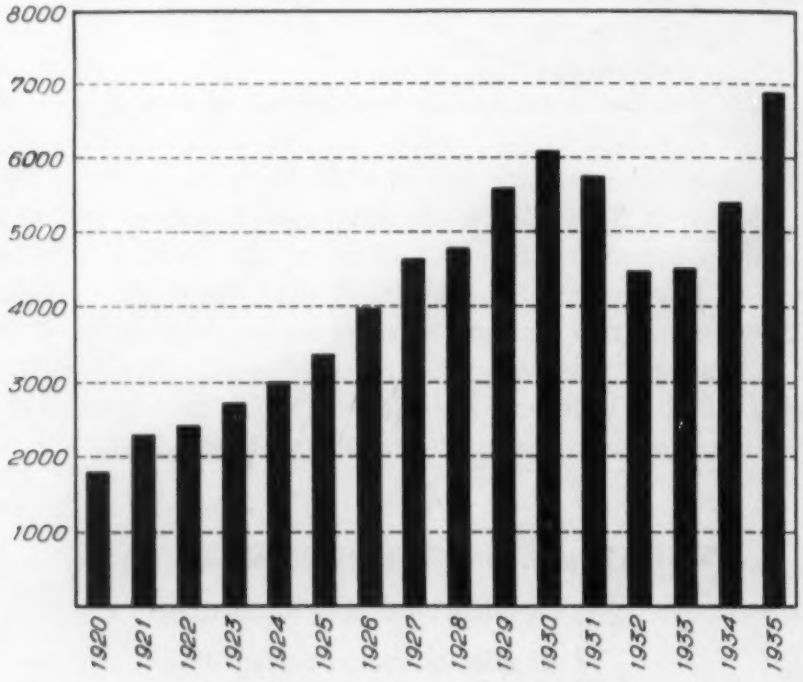
On October 1 last year the Society had a total membership of 5443. This shows an increase for the year of 1437, or 26.4 per cent.

It is interesting to note from the table included in this report that when the Society was organized in 1920 by the amalgamation of the American Steel Treaters Society and the Steel Treating Research Society at Philadelphia the membership of the combined units was 1724. During the 15 years since that date, the Society has

shown an increase in membership of approximately 5000 members.

In all of the 15 years, with the exception of 1931 and 1932, the Society has shown an increase in membership. This year, with a 26.4 per cent increase, has been the best year in the history of the Society, and while an increase of 444 members in 1921 gave us an increase of 25.7 per cent, it required approximately 1400 new members in 1935 to give us approximately the same percentage.

The tremendous increase in the membership of the Society, together with the encouraging outlook for the coming years when



Membership of American Society for Metals

the effects of the recent depression have been entirely obliterated, presents a very interesting problem to the trustees of the Society in that it may be possible that the law of diminishing returns may prompt, within a short time, the establishment of a fixed membership in the Society and a waiting list for admission to the organization.

Classification of Membership for 1935

Members	6130
Junior	282
Sustaining	446
Honorary	22
	6880

MEMBERSHIP 1920-1935

Year	Total Members	Increase	Per Cent Increase
1920	1724	....	.....
1921	2168	444	25.7
1922	2313	145	6.7
1923	2746	433	18.7
1924	3026	280	10.2
1925	3363	337	11.1
1926	4000	637	18.9
1927	4653	653	16.3
1928	4844	191	4.1
1929	5615	771	16.0
1930	6138	523	9.3
1931	5761	— 377	— 6.15
1932	4468	—1293	—22.4
1933	4470	2	0.045
1934	5443	973	21.8
1935	6880	1437	26.4

Educational Activities

The educational lecture course activities of the several chapters of the Society has been rather extensive throughout the past year. Numerous chapters have prepared their own courses of instruction in addition to the one which was prepared by the National Society under the authorship of Dr. A. A. Bates, Assistant Professor of Metallurgy, Case School of Applied Science.

The series of eight lectures prepared by Dr. Bates, entitled "Fundamentals of Ferrous Metallurgy" was published in pamphlet form containing 175 pages printed in a style similar to TRANSACTIONS, and made available to all chapters of the Society desiring to use lectures for their educational activities. The following seven chapters took advantage of this group of papers:

	Enrollment
Buffalo	110
Los Angeles	72
Milwaukee	100
New Jersey	98
Ontario	100
Indianapolis	14
Springfield	30

The cost of preparing 1500 sets of lectures together with the illustrating slides amounted to $1029.88.

Chicago presented a five-lecture course on nonferrous metals; average attendance 175.

Cincinnati in co-operation with the University of Cincinnati presented an evening course on "General Metallurgy" by G. M. Enos.

Cleveland presented a six-lecture course on "Physical Testing

of Metals" by Prof. H. D. Churchill; attendance 154. The course was open to the Canton-Massillon Chapter and 14 members took advantage of the opportunity. Also a second six-lecture course the latter half of the year on "Engineering Alloy Steels" by E. E. Thum; attendance of 140.

Detroit presented a six-lecture course on "Melting, Working, Forging, Welding and Inspection of Steels" during the first half of the year and during the second half of the year presented a six-lecture course on "Spectrographic Analysis" by Dr. E. J. Martin with an average attendance of more than 300.

Golden Gate in connection with San Francisco Evening Schools presented "Practical Metallurgy" given by H. S. Taylor. Also Beginners' and Advanced Laboratory Courses, which was limited to 20 students.

Montreal presented a lecture course on Metallic Arc Welding.

New Haven conducted an 8-lecture course on "Iron and Steel."

Philadelphia in collaboration with Temple University conducted a lecture and laboratory course on "Metallography and Heat Treatment." Also a special evening course on "Stainless Steels."

St. Louis sponsored a course on "Heat Treatment of Steel" in co-operation with The David Ranken, Jr. School of Mechanical Trades.

Tri-City presented an 11-lecture course on "Practical Course on Metals."

Washington presented a 12-lecture course on "Physical Metallurgy."

York presented 20 lectures on General Metallurgy which were given mostly by members of the York Chapter.

Pittsburgh presented three courses, i.e.:—(1) "The Structure of Metals" by Howard Scott, attendance 103. (2) "Heat Treatment of Metals" by F. H. Allison, Jr. (3) "Basic Open-Hearth Furnace" by M. W. Lightner.

During the time of the Sixteenth Annual National Metal Congress last year in New York City, James P. Gill, Vanadium-Alloys Steel Company, presented a group of five lectures on Tool Steels which course was open only to members of the Society. Two hundred and fifteen registered in attendance for this series of papers.

Metals Handbook Committee

The personnel of Metals Handbook Committee for the year

1935 is as follows: Dr. C. H. Herty, Jr., Chairman, H. J. Fischbeck, J. P. Gill, W. D. Halsey, H. B Knowlton, F B. Lounsberry, E. C. Smith, Adam Steever, and Jerome Strauss.

On April 12, 1935, the Committee held one of its regular meetings at the Headquarters Offices of the Society in Cleveland. At this meeting plans were made for the preparation and issuing of the next edition of Metals Handbook.

Ferrous Section of the Handbook

During the past year sixteen committees and thirty authors have been preparing articles for the Ferrous Section of Metals Handbook. One hundred and eighteen members of the Society have participated in this work and were selected from twenty-one different Chapters. The articles and reports that have been prepared or are in the process of preparation by both committees and authors for the Ferrous Section of the Handbook are as follows:

Completed Articles

1. Age Hardening of Iron and Steel
2. Chromium Plating
3. Hardness Test at Elevated Temperature
4. Constitution of Iron-Titanium Alloys
5. Slushing Compounds
6. Critical Points for S.A.E. Steels
7. Industrial Heating Furnaces
8. Hardness Testing
   a. Cloudburst
   b. Microcharacter
   c. Herbert Pendulum
9. Metal Cleaning by Blast Process
10. Properties of Propane and Butane
11. Copper as an Alloying Element in Steel
12. Constitution of Iron-Manganese-Carbon Alloys
13. Pyrometry (new revised article)
14. Machinability of Steels
15. Magnetic Testing
16. Constitution of Iron-Silicon Alloys
17. Chemical Analysis of Steels
18. Testing and Properties of Sheet and Strip
19. Forging S.A.E. Alloy Steels
20. Constitution of Iron-Nickel-Chromium Alloys
21. Properties of Cold Rolled Bars
22. Carbon Steels for Forging
23. Metal Cleaning by Tumbling and Burnishing
24. Testing of Tool Steels

Articles Assigned But Not Completed

1. Forging of Stainless Steels
2. Gas Carburizing
3. Heat Resisting Alloys
4. General Article on the Heat Treating of Metals
5. Impact Testing
6. Series of Welding Articles
7. Wrought Iron
8. Aluminum as an Alloying Element in Steel
9. Blue Brittleness of Steels
10. Physical Properties of Large Sections
11. Metal Cleaning by
    a. Pickling
    b. Electrolytic Pickling
12. Data on Fuels
    a. Natural and Artificial Gas
    b. Fuel Oils
13. Tool Steel Applications
14. X-Ray Radiography
15. Spectrographic Analysis
16. Macro Etching Reagents

Nonferrous Section of the Handbook

The Nonferrous Data Sheet Committee of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers in co-operation with Metals Handbook Committee has prepared a comprehensive program for the Nonferrous Section. Although this program was formulated only last March, several manuscripts have already been completed.

The personnel of the Nonferrous Data Sheet Committee is as follows: Jerome Strauss, Chairman, L. W. Kempf, N. B. Pilling, W. E. Remmers, W. G. Schneider, and E. E. Schumacher.

The nonferrous articles that have been received and those that are in the process of preparation are as follows:

Nonferrous Articles Completed

1. Constitution of Aluminum Nickel Alloy
2. Properties of Wrought 70-30 Brass
3. Brazing
4. Properties of Copper Alloy (Adnic)
5. Properties of Copper Alloy (Herculoy)
6. Properties of Copper Alloy (Ambrac)
7. Constitution of Copper-Nickel-Zinc Alloys
8. Properties of Commercially Pure Wrought Copper
9. White Gold Alloys
10. Constitution of Gold Silver Alloys
11. Properties of Lead Tin Alloys
12. Properties of Lead Base Bearing Alloys
13. Properties of Lead Antimony Alloys
14. Lead Industry
15. Forming of Magnesium
16. Riveting of Magnesium
17. Constitution of Nickel-Silicon Alloys
18. Constitution of Nickel-Cobalt Alloys
19. Constitution of Nickel-Zinc Alloys
20. Constitution of Nickel-Beryllium Alloys
21. Constitution of Nickel-Sulphur Alloys
22. Polishing of Nickel and its Alloys for Microscopic Examination

Nonferrous Articles Assigned But Not Completed

1. Properties of 27S Aluminum
2. Properties of Aluminum-Magnesium Alloys
3. Constitution of Aluminum-Chromium Alloys
4. Hot and Cold Workings of Aluminum Alloys
5. Heat Treatment of Cast Aluminum Alloys
6. Heat Treatment of Wrought Aluminum Alloys
7. Properties of 51S and A51S Aluminum Alloys
8. Properties of 25S Aluminum Alloy
9. Properties of 17S Aluminum Alloy
10. Aluminum Industry
11. Properties of 52S Aluminum Alloy
12. Properties of Admiralty Metal
13. Properties of Cast Aluminum Bronze
14. Properties of Wrought Aluminum Bronze
15. Etching of Aluminum for Metallographic Examination
16. Polishing of Aluminum for Metallographic Examination
17. Properties of 60-40 Wrought Brass
18. Properties of 80-20 Wrought Brass
19. Properties of Cast Bronzes
20. Properties of Wrought Bronzes
21. Constitution of Cadmium-Nickel Alloys

23. Properties of Nickel-Manganese Alloys
24. Soldering
25. Properties of Wrought Silicon Bronze
26. Polishing of Tin and its Alloys for Microscopic Examination
27. Etching Tin and its Alloys for Microscopic Examination
28. Properties of Tin Base Bearing Alloys
29. Physical Constants of Tin

Nonferrous Articles (Cont.)

22. Properties of Copper-Nickel-Tin Alloys
23. Constitution of Cadmium-Copper-Silver Alloys
24. Hot and Cold Working of Copper Alloys
25. Properties of Cadmium-Nickel Alloys
26. Constitution of Copper-Beryllium Alloys
27. Properties of Copper-Nickel Alloys
28. Magnesium Industry
29. Protection of Magnesium against Corrosion
30. Properties of Cadmium-Copper-Silver Alloys
31. Welding of Magnesium
32. Machining of Magnesium
33. Properties of Magnesium Forging Alloys
34. Properties of Wrought Magnesium Alloys (1.5% Mn)
35. Properties of Wrought Magnesium Alloy (4% Aluminum)
36. Properties of Magnesium-Aluminum-Zinc Cast Alloy (Al 6% and Zn 3%)
37. Properties of Magnesium-Aluminum Cast Alloy (12% Aluminum)
38. Properties of Magnesium-Aluminum Cast Alloy (8% Aluminum)
39. Properties of Magnesium-Aluminum Cast Alloy (10% Aluminum)
40. Properties of Magnesium-Aluminum Alloys
41. Tin Industry
42. Constitution of Zinc-Nickel Alloys
43. Properties of Wrought Zinc Alloys

Revised Edition of Metals Handbook

It is planned to revise Metals Handbook and issue a new book to the members sometime during the summer of 1936. The work of checking and revising articles is already underway. About two-thirds of the sub-committees and authors, who have articles in the present edition of the Handbook, have been reappointed to review their particular sections, and to determine what revisions and changes are necessary.

The preparation of the new edition of Metals Handbook places

much work and responsibility upon the members of the Metals Handbook Committee, its sub-committees and authors. These men are to be complimented upon their splendid interest and co-operation, which they are showing in the planning and preparation of the new edition of Metals Handbook.

Publication Committee

The Publication Committee for the year 1935 was made up of the following: G. R. Brophy, Chairman; Ray T. Bayless, Secretary; C. L. Clark, W. L. Cockrell, E. S. Davenport, A. E. Focke, M. H. Frommann, W. E. Harvey, T. L. Joseph, D. F. McFarland, R. F. Mehl, C. B. Sadtler, W. P. Sykes, H. S. Taylor, and Joseph Winlock.

Throughout the year and up to the present date the Committee has reviewed 41 papers, of which 33 have been approved, 7 rejected and one withdrawn by the author.

The first and only meeting for the year 1935 to date was held in Cleveland at the National Offices at 9:45 A. M., January 4th, and the following members were in attendance: C. L. Clark, W. L. Cockrell, E. S. Davenport, A. E. Focke, W. E. Harvey, R. L. Kenyon, D. F. McFarland, R. F. Mehl, C. B. Sadtler, H. S. Taylor, Joseph Winlock and Ray T. Bayless, Secretary.

The following was made a part of the record of this Committee meeting:

The members of the Publication Committee made suggestions to the Secretary as to those persons who might have technical contributions to offer at the 1935 Convention. With this list as a basis contacts were made, resulting in the technical sessions that are scheduled for this Convention. One of the chief changes in the submission of papers for consideration for the Convention was in relation to a ruling made by the Board of Trustees at their November 9, 1934, meeting in which the time limit for the submission of papers for preprinting was extended to 120 days. Therefore, the plan that was in force this year was that in order for a paper to be preprinted it must be in the National Headquarters office at least 120 days in advance of the Convention, and a paper submitted after this date but prior to 90 days would be eligible for presentation without preprinting.

The item of a symposium for the 1935 Convention was abandoned due to lack of sufficient time to organize a comprehensive program. However, a resolution was made that the Chairman consider

the advisability of arranging a symposium on the general subject of "The Plasticity of Metals" for the 1936 Convention and that he appoint a committee within the Publication Committee to formulate a plan and proceed with the securing of papers for such a symposium. This committee was formed and consists of the following members: C. L. Clark, Chairman; E. S. Davenport and D. F. McFarland, members. A meeting of this Committee was held in the National Office in Cleveland on July 8th for the purpose of making arrangements for this symposium for 1936.

Transactions

There has been published since the last annual meeting of the Society, four quarterly issues of TRANSACTIONS, namely December, March, June and September, (TRANSACTIONS ceased as a monthly publication with the September 1934 issue). The number of pages published in the four issues of TRANSACTIONS since the last annual meeting totals 1130 pages.

The TRANSACTIONS published since December 1934 contain papers presented at the 1934 Convention, together with others received during the year. The last issue of Volume 22 (December 1934) contained 12 papers and the first three issues of Volume 23 for 1935 contained 32 papers. An analysis of the editorial production of TRANSACTIONS from Volume 1 up to and including Volume 23, No. 3 (September 1935) shows a grand total of 22,126 pages.

Preprints

Thirty papers were presented before the 16th annual Convention held in New York last year (1934). For this year's Convention 30 papers have been scheduled for presentation all of which have been preprinted and distributed to those members requesting them. The total number of pages of preprints for 1934 was 620, whereas the total number of preprint pages for 1935 is 688. The number of requests for preprints this year has been approximately double that of last year.

The Review

During the past year THE REVIEW has been published as a bi-monthly, containing either 6 or 8 pages.

The September issue, which had a circulation of 16,000 among the members of all societies and divisions co-operating in the 1935 National Metal Congress, was 8 pages.

From November, 1934, to date (6 issues) 1608 column-inches were devoted to editorial matter and 465 to advertising. The amount of THE REVIEW space devoted to reports of chapter meetings was 715 column-inches, or nearly one-half of the entire space during the year.

Report of Metal Progress

METAL PROGRESS has completed a successful year. A number of outstanding articles concerning improvements in materials and fabrication properties were presented in that magazine for the first time. The high quality of authorship, illustration and typography has been steadily maintained. Due to an encouraging improvement in advertising patronage (and therefore gross income) the number of reading pages has been increased about 20 per cent, and still has enabled us to extend this useful service to the largely increased membership without involving any serious charge on the Society's treasury. The current issue for October, the special convention issue, breaks all records for advertising volume, editorial volume and gross income.

Books

The Society, without endeavoring to enter into the book publishing field, has automatically produced a number of very interesting and outstanding publications. The interest in these publications, as indicated by their sales, has justified the Society in making a distribution of the information contained therein.

So far the Society has produced, and successfully distributed, the following books, a number of which are in the second edition:

"Lectures on Steel and Its Treatment," by John F. Keller

"Principles of Heat Treatment of Steel," by the Bureau of Standards

"Heat Treatment, Uses and Properties of Steel," by H. B. Knowlton

"The Constitution of Steel and Cast Iron," by Frank T. Sisco

"Nitriding Symposium"—a collection of A.S.M. convention papers

"Application of Science to the Steel Industry," by W. H. Hatfield

"Inclusions in Iron," by C. R. Wohrman

"Grain-Size Symposium," a collection of A.S.M. convention papers

"The Quenching of Steels," by H. J. French

During the past year the Society has issued the second edition of the Book of Stainless Steels, the first edition of 2000 volumes having been sold in less than a year. The new edition gave the various contributors a chance to bring their portion of the book up to date with the result that a much enlarged second edition was delivered from the printer early in 1935. Sales continue to be very gratifying.

Another publication of the year is the Tool Steel Lectures presented by Mr. J. P. Gill at the New York convention. Also published was a limited autographed edition of a "Metallurgical Dialogue" by Dr. Albert Sauveur.

The books in preparation for publication and soon to be off the press include the lectures presented by Dr. M. A. Grossmann at the present convention, and an Index of Engineering Alloys containing the trade names, manufacturers, chemical analyses and uses of over 7000 engineering alloys, by Norman E. Woldman and Professor A. J. Dornblatt; and also a series of charts entitled, "The Steel Physical Properties Atlas" by C. N. Dawe.

It is interesting to note from an analysis of the financial statement presented by Treasurer Gathmann today that the sale of books accounted for an income of approximately $6000.00 last year.

The Exposition

The National Metal Exposition, which opened for the 17th time last Monday, indicates that this activity of the Society still continues to represent an outstanding advertising and merchandising opportunity, and that it is so recognized by manufacturers is indicated by the fact that this year there are 230 exhibitors, representing a total income for space of $62,170.

The income in round figures for the expositions since 1928 is as follows:

1928—Philadelphia	$62,460.00
1929—Cleveland	62,420.00
1930—Chicago	45,650.00
1931—Boston	39,360.00
1932—Buffalo	22,890.00
1933—Detroit	29,440.00
1934—New York	42,100.00
1935—Chicago	62,170.00

The present exposition represents an increase of 50 per cent over the show held in New York last year. It surpasses greatly the

shows for the last five years, and is within $290.00 of the largest show in the past 8 years.

Conclusion

When one observes the tremendous and remarkable increase in membership the Society has sustained during the past year, the question presents itself as to why such a condition should be prevalent, when all are conscious of the fact that while business conditions have shown a decided improvement we are not yet in the care-free, plenty-of-money period of the years previous to 1930.

While the factors in the growth of an organization are intangible items, it may be interesting to record the facts which have apparently contributed to the great influx of new members.

No. 1 might be the steadily growing influence and recognition of the work being accomplished by the chapters of the Society and the services from headquarters.

Another factor from which results are directly apparent has been the large amount of educational activity carried on by the various chapters when they have rightfully required membership in the Society in order to enjoy the privileges of this extension work.

A factor which should not remain unnoticed is that of the change of the name of the Society. Its immediate acceptance not only by the members but by the metal fraternity in general has led to a better recognition of the field of service which has always been covered by the A.S.M.

The factor which beyond all doubt has been most contributory to the outstanding and exceptional growth of the Society has been the activity and loyalty of the Society's friends, its members, which are numbered among the thousands.

Every member is enthusiastic in his membership and seems eager to share his benefits with his fellow-worker. With such unselfish devotion by the established members of the Society, only the most optimistic outlook appears on the horizon.

ELECTION OF OFFICERS

B. F. SHEPHERD, *President*

I have the pleasure to report that in accordance with the constitution of the A.S.M. the President received prior to March 1 of this year suggested candidates for the Nominating Committee from

all the local chapters of the Society entitled to make nominations. From the list of eligible candidates suggested, I appointed the following Nominating Committee of seven:

J. P. Gill, Pittsburgh chapter—chairman
R. T. Porter, New Haven
T. J. Black, Canton-Massillon
S. L. Hoyt, Milwaukee
S. A. Silbermann, Indianapolis
F. A. Elshoff, New Jersey
D. M. Fraser, Ontario

The names of the members of the Nominating Committee were published in the March REVIEW.

The Nominating Committee responded to the call of its chairman and held a meeting in Pittsburgh during the third full week in May and reported immediately the selection of the following candidates for the offices indicated:

For president for one year—R. S. Archer
For vice president for one year—E. C. Bain
For treasurer for two years—W. P. Woodside
For trustee for two years—R. L. Kenyon
For trustee for two years—S. C. Spalding

The report of the Nominating Committee was published in the May REVIEW.

I have been notified by the secretary that no additional nominations were received prior to July 15 for any of the vacancies occurring on the board of trustees. Consequently, the nominations were closed. I shall now call upon the secretary to perform his duty as prescribed by the constitution.

W. H. EISENMAN, *Secretary:* Mr. President, since no additional nominations were received prior to July 15, 1935, for any of the vacancies on the board of trustees of the American Society for Metals, I herewith, in compliance with the provision of the constitution, cast the unanimous vote of all of the members of the Society for the election of the following candidates:

For president—for one year—R. S. Archer
For vice president—for one year—E. C. Bain
For treasurer—for two years—W. P. Woodside
For trustee—for two years—R. L. Kenyon
For trustee—for two years—S. C. Spalding

B. F. SHEPHERD, *President:* Since all the provisions of the constitution have now been performed, I herewith declare the candidates named to have been duly and unanimously elected for the term and office specified, and the term of office of each officer just elected shall begin on the day following the close of this annual meeting.

The Annual Banquet

The Society played host to more than eight hundred members and guests at its annual banquet held Thursday evening, October 3, in the Ballroom of the Palmer House. Several hundred executives of important steel producing companies were in attendance. Seated at the speakers' table were the following: W. A. Irvin, president of the United States Steel Corporation; B. F. Fairless, president of the Carnegie-Illinois Steel Corp.; I. Lamont Hughes, executive vice president, Carnegie-Illinois Steel Corp.; Walther Mathesius, manager of operations, Carnegie-Illinois Steel Corp.; G. C. Kimball, vice president, Carnegie-Illinois Steel Corp.; Dr. H. C. Urey, Columbia University; S. C. McAllister, president, International Harvester Co.; Emil Gathmann, president, Gathmann Engineering Co.; W. H. Phillips, vice president, Molybdenum Corp. of America; Dr. Zay Jeffries, Aluminum Co. of America; T. E. Barker, president, Accurate Steel Treating Co.; W. P. Woodside, vice president, Climax Molybdenum Co.; Dr. A. E. White, director of research, University of Michigan; R. H. Cabell, president, Armour Co.; R. S. Archer, president-elect, A.S.M., Republic Steel Corp.; H. B. Knowlton, International Harvester Co.; R. L. Kenyon, American Rolling Mill Co.; S. C. Spalding, American Brass Co.; H. W. McQuaid, Republic Steel Corp.; Dr. T. D. Yensen, Westinghouse Electric and Manufacturing Co.; N. A. Ziegler, West Penn Electric Co.; Dr. G. B. Waterhouse, Massachusetts Institute of Technology; Dr M. A. Grossmann, Carnegie-Illinois Steel Corp.; E. T. Lawless, manager Palmer House; K. H. Hobbie, Driver-Harris Co.; W. H. Eisenman, secretary, American Society for Metals.

Robert S. Archer, president-elect of the Society, presided at this banquet meeting due to the illness of President B. F. Shepherd. In addressing those in attendance at this outstanding dinner meeting, Mr. Archer said in part:

"Members of the American Society for Metals and honored guests:

"We welcome you to this, our Seventeenth Annual Banquet. Just seventeen years ago this month, the first convention and exposition of the Society was held here, in Chicago, at the Seventh Regiment Armory Building.

"It is indeed a source of pride and pleasure to all of us to recognize and observe the growth and advancement of the Society. Not

only in its number of members but also in the size and quality of the exposition.

"We have returned to Chicago on two other previous occasions. The second time was in 1926 and again in 1930. Chicago makes a most acceptable host city, and it is a pleasure to us to have the opportunity of being in this city again.

"I would like to express the appreciation of the Trustees and the Membership of the American Society for Metals to the Institute of Metals, and the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers, The American Welding Society and the Wire Association for their hearty co-operation in making this Seventeenth National Metal Congress such an outstanding success.

"I am going to take the privilege now of introducing the gentlemen at the Speakers' Table. However, I shall not introduce at this time those who are sitting at the Speakers' Table who will be called upon later to participate in some of our activities.

"While I know each and every one of them will merit from you a very cordial reception, I should like to request that you refrain from applause until I have finished introducing all of them, and then we will accord to them the grand salute of good fellowship."

At this point the guests at the speakers' table were individually introduced to the audience.

Presentation of the Past President's Medal

In continuing president-elect Archer said:

"It now becomes my privilege and duty to present the Past President's Medal to Mr. W. H. Phillips. For many years Mr. Phillips has worked tirelessly in the interest of the Society. He has been a member of the Society since its inception, and has served the Pittsburgh Chapter of which he is a member, loyally and faithfully. He has served as a member of the Board of Trustees of the National Society for a period of two years. He served as Vice President for one year, and last year very capably performed the duties as President of the American Society for Metals. The Past President's Medal is now awarded to him in sincere appreciation of his splendid services to the organization."

Henry Marion Howe Medal Award

"Every year, some time prior to this banquet, we start to select the outstanding paper presented before the Society and published in

TRANSACTIONS during the year. Four Committees are appointed consisting of three men each. These Committees each cover three months publications, selecting the two best papers of that quarter. The Final Award Committee of three members selects from the papers thus chosen one paper, the author of which is presented the Henry Marion Howe Medal.

"This year we are pleased to present the Howe Medal to Dr. T. D. Yensen of the Westinghouse Electric and Manufacturing Company, and N. A. Ziegler of the West Penn Electric Company, who as co-authors presented before the Society a paper entitled "Magnetic Properties of Iron as Affected by Carbon, Oxygen and Grain-Size" and which was published in the June, 1935, issue of TRANSACTIONS."

Albert Sauveur Achievement Medal Award

"As outlined at the annual meeting last year we, as a Society, are justly proud of our Campbell Memorial Lectures and our Howe Medalists, and the contributions they have made to metallurgical literature. We have felt, however, an outstanding achievement in the field of metallurgy should receive special recognition—so after a great deal of deliberation we have created a new recognition known as the Albert Sauveur Achievement Award. This award was established in honor of Dr. Sauveur who has contributed so richly and inspired so universally, workers of all types in the field of metallurgy. It was highly appropriate that last year the award was made to Dr. Albert Sauveur in whose honor it was created.

"The past Presidents of the Society are all members of the Committee of Award. This year, the Chairman of that Committee is Dr. Albert E. White, Director of the Department of Engineering Research at the University of Michigan.

"It is now my pleasure to introduce to you Dr. A. E. White, Chairman of the Committee on Award and also the First President of our Society, to present the candidate for this honor:"

In presenting Dr. Jeffries for this award, Dr. White said:

"On behalf of the Past Presidents of the American Society for Metals, I have the honor to present to you Dr. Zay Jeffries as the recipient, for the year 1935, of the Albert Sauveur Achievement Award.

"His career has been one of steady progress and development in technical, consulting and business fields. The metallurgical pro-

fession throughout the entire world knows of his broad generalizations regarding the laws of grain growth in all metals, including the phenomenon of germinative grain growth. He has pointed out the effect of obstructing agents such as thoria in metals like tungsten.

"He also brought out a generalized theory of the hardening of metals known as the "Slip Interference Theory." Likewise, he has made important contributions on the effect of temperature, deformation, and grain size on the properties of metals.

"He assisted materially in reducing the manufacture of tungsten wire to a scientific basis which has been such a boon to mankind through its use in electric lamps. His scientific work has led to important applications in the heat treatment of steel and to improving the red hardness of high speed steel. His contributions in the nonferrous field are as well known as they are in the ferrous, through his work in the aluminum industry. In this field he has made important improvements in the art of casting aluminum alloys in permanent molds, as well as being responsible for having brought out many new alloys and heat treating processes which have found large useful applications. More recently he has been engaged in the work of improving and extending the commercial application of sintered tungsten carbide tool materials, as well as the new iron-cobalt-tungsten tool alloy known as No. 548.

"As a teacher, investigator, and director of large and important research programs his life has been one of outstanding fullness. Yet withal he has given unstintingly of his time to the humblest investigator who came to him for help. He has also shown unsparing devotion to the work of technical organizations, especially to the American Society for Metals, of which he is a Past President.

"It is indeed a privilege and an honor to present to you, Mr. President, Dr. Zay Jeffries for the Sauveur Achievement Award; for the Society in honoring him, honors itself."

In accepting the award Dr. Jeffries responded as follows:

"Mr. Chairman, Ladies and Gentlemen:

"I am naturally much pleased and gratified to be the recipient of this high honor. It is especially gratifying to have it presented by my former associate in research work and in writing, Mr. Archer.

"In accepting this Award, it is appropriate to point out that any achievements attributed to me must be shared by others and due allowance should be made for fortuitous circumstances. In the first place, the background of our great heritage provides the uncrushable

foundation upon which each of us may add his bit. Then the schools, technical societies and industrial corporations, large and small, provide us with educational, physical, and financial equipment which makes it relatively easy to unlock many of nature's secret doors.

"Finally, one's associates give both direct help and inspiration. In this respect I have been most fortunate. Among the older men with whom I have had the good fortune to be associated may be mentioned Professor C. H. Fulton, J. V. N. Dorr, Professor H. M. Howe, Professor Bradley Stoughton, F. N. Speller, and, as a pupil, Professor Sauveur in whose honor this Award has been established. Among my other past associates are some of the younger but outstanding metallurgists including S. L. Hoyt, R. S. Archer, E. C. Bain, Ivan McCorkle, C. R. Austin, Wm. Chancellor, and E. C. Wright. Among my present associates may be mentioned such prominent metallurgists as F. C. Frary, E. H. Dix, L. W. Kempf, W. L. Fink, T. D. Stay, K. R. VanHorn, and W. A. Dean of the Aluminum Company of America; and B. L. Benbow, W. P. Sykes, T. S. Fuller, W. E. Ruder, F. C. Kelley and Gerald Brophy of the General Electric Co.

"I hope that these living associates, past and present, and many more not mentioned by name, will feel that I am receiving this Award in part as their custodian.

"I wish also to express my gratitude to another group of associates, namely, the officers, past and present, of the American Society for Metals. This Award will, I am sure, encourage me to keep an active interest in metallurgy and serve as a reminder to be a friend to all metallurgists.

"Now I have a pleasant task to perform. Professor Sauveur himself received the initial Award of this honor a year ago in New York. As might have been expected, he made a few gracious but modest remarks and sat down. I shall try very briefly to sketch his place in the metallurgical industry.

"First, there was metal art which gave birth to the metal industry. The knowledge, slowly and painfully gained, was passed on from generation to generation. Occasionally accidental discoveries would be made. There was little understanding of what was being done. This procedure went on for centuries. Finally, metal art and metal industry gave birth to an offspring, metal science. So lusty and precocious has this child become that it has in recent years been guiding both parents sometimes without much ceremony.

Not that the parents have become less—in fact metal art is greater than ever before and the metal industry has grown so rapidly that it astounds even those closest to it.

"It is not generally realized, for example, that the world's new metal production since the beginning of this century has been greater than that for the whole of previous history. When the large recovery of secondary and scrap metal is given consideration, the metal industry of the twentieth century so far has substantially exceeded that of all previous time. New metal production alone has been as much as 100,000,000 tons in a single year.

"The industry is in a quantity phase and is rapidly merging into a quality phase based on metal science.

"In the early 1890's, here in Chicago, Professor Sauveur fired, not the first, but an early and a most important metal science gun. He presented a paper on the heat treatment of steel before the American Institute of Mining Engineers, which had far-reaching effects. It is not a coincidence that the period of prodigious growth of the metal industry was the one in which metal science also grew by leaps and bounds. There is hardly a pound of metal used today that does not bear the imprint of the metal science hand either by the producer or the consumer, or both. Indeed, the active interplay between metal art, production, and science on the one hand, and the producer and consumer on the other, constitutes our great metal industry. Important as has been metal science in this development in the past, it promises to be an even more important factor in the future.

"It is in this field that Professor Sauveur has made his great contributions. To build this metal science structure, two things have been necessary, (1), new ideas and leadership in sound thinking, and (2), the training of men to experiment, analyze, interpret, and carry on. He has provided many new ideas and has been a great teacher. If judged by his accomplishments in either field, his rating in the metallurgical world would be high. Judged by his accomplishments in both fields, coupled with the fine character and friendly spirit of the man, his record is matchless.

"Majestically posed in this great metallurgical frame, Professor Albert Sauveur, still living and active, looks out serenely on the teeming world justly deserving the unofficial title 'Dean of Metallurgists'."

Address by W. A. Irvin

Following this presentation the guest of honor and speaker of the evening, W. A. Irvin, president of the United States Steel Corporation, gave his outstanding address which is printed in full herewith.

"The pleasure I derive in being with you on this occasion is both genuine and unalloyed. It is always a privilege to meet with so many friends and associates at any one time, but particularly pleasant to partake of those activities in which all of us are making common cause. When I recall the meetings of the "Steel Treaters" which I attended years ago and compare the early position of the Society with its present eminence and record of accomplishment, there is good reason to commend the American Society for Metals, most heartily, upon the part it has played in advancing the interests of the metals industry. Stature and influence are not attained by accident—they bear evidence of a worthy cause, an abundance of hard work, intelligent planning, and the performance of real service to the membership, year by year. My compliments to you as an organization, and to the members as such.

"Some time after the close of the French Revolution a visitor from England inquired of a French acquaintance, 'What did you do during the Reign of Terror?' 'I survived,' he said. During the five or six years just past the problem of survival has been an important one with many organizations and enterprises throughout the world. The rapid deflation of business activity in the early 1930's imposed a heavy burden upon industry, bringing into jeopardy not only the social well-being of large numbers of its workers, but the integrity of much of its capital structure as well. A complex mechanism designed and built to operate effectively at a high rate was suddenly confronted with the necessity of dwarfing its operations to a fraction of normal capacity, without thereby stopping altogether. Men and machines were thrown out of their respective strides, as both human and mechanical power entered a period of enforced inactivity.

"Producers of metals shared in the common lot. In all periods of depression the demand for capital goods, especially the heavier products, is unusually low. For evidence on this point one needs look only at the figures for annual steel production, to visualize the extent to which the contraction took place. In 1928 the steel industry of the United States produced more than fifty million gross tons

of ingots. This figure was increased by about four and one-half million gross tons in 1929. Then followed three years in which the shrinkage exceeded thirteen and three-quarter million tons per annum, until the low point of approximately thirteen and one-half million tons was reached as the total production for the year 1932. So much for the descending scale. Fortunately for all of us the figures are higher now, and we are hopefully estimating; with considerable assurance, an output of more than thirty-two million gross tons of ingots for the current year. Those of you who are accustomed to predict long-range trends by the aid of carefully constructed graphs, must have realized by this time that at least one portion of the "S" curve relating to steel, has recently passed through a corrugating machine.

"The foregoing statistics have been recited, not because at first glance their inevitable comparison with figures for other recent periods will add anything to the joy of this occasion, but because they do tell a story which carries with it some reassuring implications. The bare fact that we are on the ascending side of the production-curve is encouraging. Again, we have learned, in these lean years, something useful about the stamina and flexibility of our industry, painful though the process has been. In another direction, statistically we are led to believe that if the average ingot production for the ten-year period ending with 1929, amounting to 41,500,000 gross tons per annum, indicates even approximately the position of the steel-producing industry with respect to the demands of the trade, there should soon be considerable room for increased production over that of our present rate, in view of the low average applying to the past five years. Certainly a fair proportion of this average represents deferred maintenance and replacement, therefore it should enter the picture once again as an addendum to whatever normal demand is developed.

"Man-made economic measures may or may not be found which will accelerate the rate of increase in business, but reasoning with figures fails to uncover any natural barrier to the long range opportunity for improvement, in which all essential products should share. Those of us who are interested in the outlook for metals are watching the possible influence which may be exerted by nonmetallic competitive products, as an offset to the anticipated breadth of our markets. Moreover those of us who are particularly concerned with the outlook for ferrous metals have taken cognizance of published state-

ments relating to the passing of the 'Age of Steel.' Without any intention of creating an impression of smugness, or of imputing a position of impregnability to any product now in use, we conclude that there is good reason for each of us to press along the several roads of improvement for the metals which have been occupying our attention, in the assurance that there is room for all of them. The 'age' of this, and 'age' of that, may be convenient and significant words with which to identify certain mile posts in the march of civilization, but they fall short of measuring some of the economic factors in which we are most interested. For example, no one would think that the use of stone fell into the discard with the passing of the Stone Age. Bronze is with us in larger quantities and in more useful varieties than it was when the ancient races of the Bronze Age depended upon it for their principal implements of war and peace. More candles are made and burned today than were used, in equivalent periods of time, to light the homes and buildings of our ancestors. We members of this branch of the metals industry are far from the point of conceding that the end of the Age of Steel is in sight.

"To enumerate here and now even the most important applications of steel, in the interest of supporting some of the foregoing statements, would be the equivalent of levying a nuisance tax upon your spirit of forbearance. The elimination of this versatile metal, from certain sectors, is too remote for immediate discussion. On the other hand there may be an interest in reviewing a few of the fields in which the enlarged use of steel, or its adjustment to new conditions, is receiving considerable attention. Streamlined passenger trains, constructed of alloy steel, are relatively novel, but are finding a logical place in the sphere of transportation. Data obtained thus far indicate that the amount of steel used in constructing these trains is not just so much taken for the regular tonnage requirements, but that travel is actually being increased by the new facilities. A market for various grades of high tensile alloy steels seems to be in the making as a result of this development. Similar steps are being taken with respect to street cars, trucks, and buses. In another field of transportation, namely aviation, the prospect of a sizeable market for special steels is very promising.

"In an important way, attention is now being directed to the more extensive use of steel in the construction of the superstructure of ships. Reduction of fire hazard is a prime consideration here,

although appearance and reduction in weight are also attractive possibilities.

"Office partitions of steel are not a new commodity in this country, but the furnishing of complete interiors in a manner to combine utility with artistic treatment is a more recent outgrowth of the original idea. A little farther along this line is the steel house, or more properly, the residence in which steel is used wherever proper advantage can be taken of its particular properties. Already a number of meritorious systems of construction are well under way, and we know that more are to follow. The potential market for steel in this field is one of most attractive proportions.

"An interesting new application of steel which has likely come to your attention within the past year is the container recently developed for beverages. Without standing upon tradition and custom, the public has readily accepted this tin container because of the superior service it performs, and once again the doors are opened for an enlarged consumption of steel in the form of tin plate.

"Examples might be multiplied, but enough has been said to indicate that in the development of new trade requirements, and in the constant shifting of the old, there is an important place for steel. It is our duty and responsibility to keep it so.

"The organic strength of the technical side of the steel industry, in both its producing and consuming branches, is well illustrated by the advances which have been made during recent years. The following examples will assist in elaborating upon this point:

1. In many quarters new and improved alloy steels have appeared, including the so-called high tensile group and certain members of the stainless family.

2. Controlled grain-size, dependent upon the careful regulation of many factors involved in making the steel, is now a commercially established feature, affecting numerous products of the industry.

3. The interaction of slag and metal in the open-hearth furnace is better understood, thanks to the large amount of research work which has been done on this subject. Equilibrium, a word heretofore confined to laboratory quarters, is now frequently heard on the charging floor.

4. The all important deoxidation process has been further investigated and reactionalized as a necessary complement to the other features mentioned.

5. Non-aging steel has become a factor in meeting certain trade requirements.

6. Improvements in methods of heat treating and physical testing—the results of organized research—have been so numerous and important that only a group of experts, such as those now present, could possibly comprehend their full significance.

7. Implements for the closer and more effective control of processes have been devised both within the industry and by its suppliers, so that in this direction also, the happy union between art and science is working for the betterment of all.

"In the adaptation of improved mechanical equipment, the mention of a relatively few examples will serve to illustrate the trend of developments. Hot strip mills, along with cold reduction mills, probably stand at the head of the list, at least in point of size and attraction of widespread popular interest. Die rolling, electric welding, improved seamless tube mills, and furnaces for heating steel in controlled atmospheres, are performing new services in their respective fields. In all of these examples, which undoubtedly are matched by their counterparts in other lines of the metals industry, we see tokens of continual advancement, and the promise of progressively modern products to meet modern requirements. Evolution and development must continue, if the success of tomorrow is to be greater than the achievement of today.

"Stultifying as have been the effects of the depression in some directions, it is thus gratifying to note that in others they have not prevailed over human ingenuity and technical advancement. It almost goes without saying that the productive processes of industry are still primarily dependent upon brains, regardless of how well our plants may be equipped with mechanical devices. Men construct, guide, and operate machines; they uncover natural laws, originate ideas, devise methods, and make decisions; without their direction and control the application of horsepower and other physical agencies would be futile. Metals in production and consumption have always attracted the interest of men, and the metals industry now recuperating from the effects of economic ills is fortunate in the undiminished zeal of its devotees and experts, able and willing to carry their improved and improving products into new fields of service for mankind."

Table V

The Effects of Etching Reagents Upon Nonmetallic Inclusions in Steel (Cont.)

Type	Alcoholic Stannous Chloride 10 min.	20% Hydrofluoric Acid 10 min.	Alcoholic Hydrochloric Acid	1% Ferric Chloride in Alcohol 5 min.	Azide-Iodine Reagent	Alkaline Permanganate
FeS	No effect	All removed	1 min. no effect, 5 min. removes all	No effect	Stained gray in 5 min.	Blackened (2)
MnS-FeS High Mn	No effect	All removed	1 min. removes medium and small. 5 min. removes all	No effect	Some removed in 60 sec., others not removed in 10 min.	Darkened (1)
MnS-FeS Low Mn	All removed or blackened	All removed	1 min. removes gray, 5 min. removes all	No effect	FeS stained gray. MnS darkened or removed.	FeS — rich black. Mns—rich dark (1)
Cr_2S_3-FeS	No effect	All removed	5 min. no effect	No effect	5 min. no effect	No effect
Mg_2S_2-FeS	All removed	All removed	1 min. no effect, 5 min. removes tan. No effect on eutectic	No effect	No effect on tan or eutectic in 5 min.	Tan darkened. No effect on eutectic (1)
Ti_2S_3-FeS	Blackened	All removed	5 min. no effect	No effect	No effect on tan or eutectic in 5 min.	Tan darkened. No effect on eutectic (1)
TiS_2-FeS	No effect	All removed	5 min. no effect	No effect	5 min. no effect	Darkened (1)
FeO	All removed	All removed	1 min. no effect, 5 min. removes all	Darkened slightly	No effect	No effect
Mno-FeO	No effect	All removed	All removed in 2 min.	Darkened slightly		
Chromite	No effect	No effect	No effect in 5 min.			
FeO-SiO_2	No effect	All removed	No effect in 5 min.			
MnO-SiO_2	No effect	All removed	All removed in 5 min.			
Al_2O_3-FeO	No effect	No effect	No effect in 5 min.			
CaO-SiO_2	No effect	All removed	No effect in 5 min.			
FeO-FeS	Gray removed eutectic darkened		1 min. badly attacked 5 min. removes all	All darkened considerably Gray more than tan	5 min. no effect	No effect
MnO-FeO FeS-MnS High Mn	Plain removed No effect on eutectic		Completely removed in 2 min.			
MnO-FeO FeS-Mns Low Mn	All removed		Completely removed in 2 min.			
Cr_2S_3-FeS Cr_2O_3-FeO	No effect		5 min. some inclusions attacked, others not			
Al_2S_3-FeS Al_2O_3-FeO	No effect		Some badly attacked, most blackened in 2 min.			
Cr_2S_3-FeS Cr_2O_3-FeO	No effect		2 min. badly attacked			
FeO-TiO_2 FeS-TiS_2	Needles are removed		5 min. no effect			
TiN	No effect	No effect	5 min. no effect			
ZrN	No effect	Yellow cubes badly attacked	5 min. no effect			

NOTE: (1) One minute polishing removes etching effect. (2) One minute repolishing does not remove etching effect.

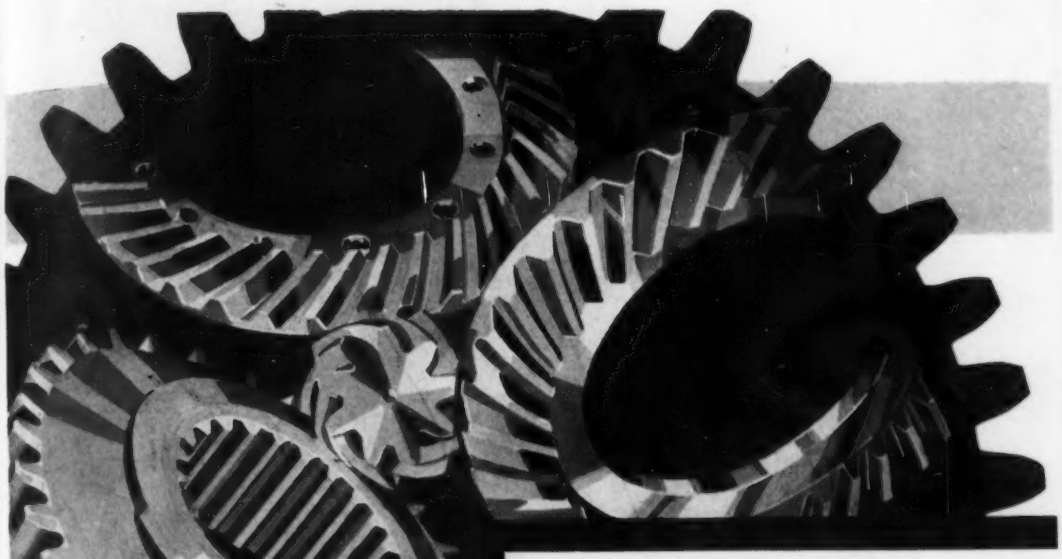
ERROR CORRECTED

In the September, 1935, issue of TRANSACTIONS, was published Part II of "Nonmetallic Inclusions in Steel" by Stephen F. Urban and John Chipman. In printing Table V on page 667 the numerals identifying the type of inclusions were omitted thus making it diffi-

cult to interpret the table. We are therefore reprinting this table with these identifying marks so that it may be superimposed upon the page in your September 1935 issue of TRANSACTIONS.

The paragraph on page 656 starting with "A summary of the heats and their analyses" . . . up to the heading "Effect of Sulphide Inclusions on Forging" should precede the second paragraph on page 645.

This is a printer's error on arrangement but contains no typographical inaccuracies.



STEELS
That Do A
BETTER JOB

Today is the day of "tailor-made" steels . steels made to meet the requirements of specific applications. Republic's Improved Series of 3100 Steels is an excellent example of this new trend in steel making. » » » Manufacturers of transmission gears, differential gears, suspension parts, king pins and similar carburized, quenched or oil hardened applications wanted better steels . . steels of greater hardenability . . . steels that would develop a tougher core and a better case . . steels that could more readily be conditioned for machining. They wanted a steel that would give even better results than the higher priced alloy composition which they were then using. » » » Today, many manufacturers have improved their products and reduced their costs with these new Republic Improved 3100 Series. In analyses these improved 3100 Steels do not differ from standard S.A.E. compositions. But, made to new methods of metallurgical control, they are finer grained and markedly superior in performance. This is a typical instance of Republic's endeavors to develop more economical products for users of steel. » » » It will pay you to investigate the possibilities of Republic's Improved 3100 Series.

Republic Steel
CORPORATION
ALLOY STEEL DIVISION, MASSILLON, OHIO
GENERAL OFFICES: YOUNGSTOWN, OHIO

FOR THE MODERN METALLURGICAL LABORATORY

Fisher always devotes much time to the design and manufacture of better metallurgical laboratory equipment.

An accurate and convenient optical pyrometer, an improved Brinell Hardness Tester, and complete equipment for grinding and polishing specimens are among the Fisher products performing satisfactorily in metallurgical laboratories throughout the world.

Complete equipment for the analysis of iron, steel, and nonferrous metals is illustrated and described in "Modern Laboratory Appliances," Fisher's new catalogue.

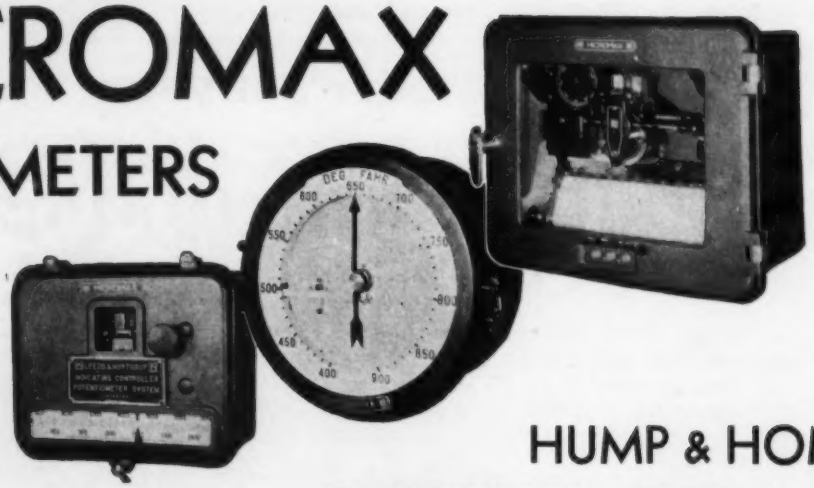
We are agents for Zeiss metallographical equipment and are now demonstrating the 1936 model Neophot.

FISHER SCIENTIFIC COMPANY

711 Forbes Street **Pittsburgh, Pa.**

MICROMAX
PYROMETERS

Indicating
Recording
Controlling



HUMP & HOMO ELECTRIC FURNACES
for
Hardening, Tempering, Annealing and Nitriding

In the Hump Vapocarb Furnace tools and dies are hardened with complete control of the three basic factors which determine heat-treating quality and costs. Hump control shows the hardener exactly when to quench. Automatic control of rate of heating holds distortion within normal tolerances. Vapocarb atmosphere prevents scale, pits and decarburization.

For tempering and low-temperature annealing, two types of automatically-controlled Homo furnaces are available: one specialized for dense loads . . . rivets, bolts, etc.; the other for more open loads . . . dies, tools, etc. . . .

Homo Nitriding furnaces enable the heat-treater to produce extremely hard surfaces on steel parts. Ho-Hump Multi-purpose furnace hardens and tempers as well as nitrides.

For regulation of heat-treating temperatures:

Micromax Strip-Chart (Model S) Recorder or Recording Controller. Records temperatures of one, or up to sixteen, points on an open-scale, strip-chart. Can be equipped for simple or elaborate automatic signals or controls.

•

Micromax Round-Chart (Model R) Indicating Recorder or Recording Controller. Giant indicating dial, readable from a distance. Also records on a circular chart with straight radial ordinates. Can be equipped for signals or simple controls.

•

Micromax Indicating and Non-Indicating Controllers. For any control problem, simple or intricate, where no record is needed. Indicating type shows temperature on a bold scale.

DETAILS ON REQUEST

LEEDS & NORTHRUP

LEEDS & NORTHRUP CO.
4960 STENTON AVENUE
J-620-(2) PHILADELPHIA, PA.

Dr. Albert Sauveur

"Dean of American Metallurgists," presents a

Metallurgical Dialogue

(Autographed by Author)

A unique and informal method of presentation wherein a master answers his pupil's question as to "why steel hardens when plunged red hot in cold water" is utilized by Dr. Sauveur, Gordon McKay Professor of Metallurgy and Metallography in Harvard University, in this fundamental discussion of steel metallurgy and metallography.

The questions asked by the pupil during the course of the dialogue lead to many subjects such as red shortness, alloy steels, cold work, high speed steel, corrosion, and stainless steels. Valuable historical material and a complete review of the various theories of hardening steel are included. Bound in cloth, 200 pages, 5½x8in., 12 illustrations.

Price — $3.00

Send your order and check to

AMERICAN SOCIETY FOR METALS

7016 Euclid Ave. Cleveland, O.

"DOING ONE THING WELL"

INHIBITORS

without Salt or Any "Dope"

NEP 100% POWDER NEP No. 22

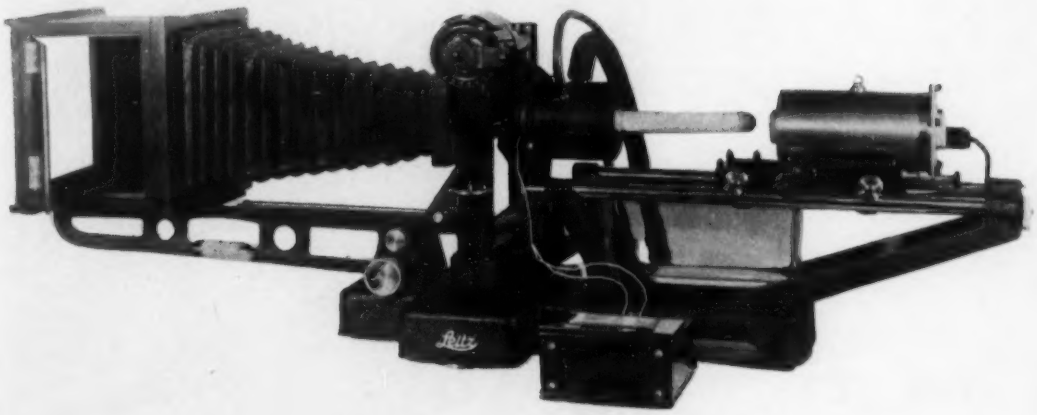
SUM-FOAM

The Wm. M. Parkin Co.

Chemical Engineers in Steel PITTSBURGH, PA.

A NEW AUTOMATICALLY RECORDING

LEITZ DILATOMETER



FOR thermal analysis of metals, determination of critical points and coefficients of expansion. Expansion-temperature curves can be automatically recorded with highest accuracy. The instrument combines simplicity of handling, compactness, highest precision and low price. The great sensitiveness in recording the minutest volume changes, the unbelievably low friction in all bearings and the optical precision transmission system make the equipment especially valuable for every Metallurgical Research Laboratory.

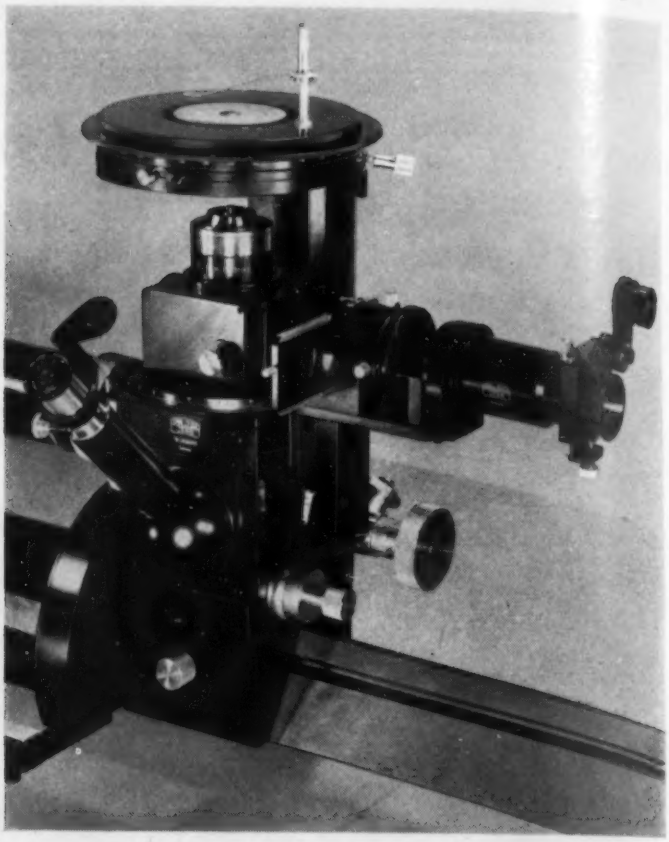
★

E. LEITZ, Inc.

60 EAST 10th STREET NEW YORK CITY

Branches:

WASHINGTON, D. C.
CHICAGO, ILLINOIS
LOS ANGELES, CALIF.
SAN FRANCISCO, CALIF.



THE NEW

ZEISS METALLOGRAPH "Neophot"

As an improvement over previous models, there is offered in the new Zeiss Metallograph a combination of advanced equipment for observation and photography with bright field and dark field illumination and polarized light, with the most flexible accessories for macro-photography. With 5″ x 7″ or 8″ x 10″ camera.

Write for literature

E. H. Sargent & Co., 155 East Superior St., Chicago

SARGENT

E.H.SARGENT & CO. CHICAGO

LABORATORY SUPPLIES

AMERICAN SOCIETY for METALS

Standing Committees—1936

CONSTITUTION AND BY-LAWS COMMITTEE

GEORGE R. LONG, Chairman '36
Frigidaire Corp.
Dayton, Ohio

George J. O'Neill, '37
Pa. Gas & Electric Co.
York, Pa.

Clyde Williams '36
Battelle Memorial Institute
Columbus, Ohio

L. F. Fitzpatrick '37
Flexible Shaft Co.
Toronto

Sam Spalding, (Ex Officio)
American Brass Co.
Waterbury, Conn.

L. D. Hawkridge '38
Hawkridge Bros. Co.
Boston

FINANCE COMMITTEE

W. P. WOODSIDE, Chairman
Climax Molybdenum Corp.
Detroit

Zay Jeffries '38
Aluminum Co. of America
Cleveland

W. S. Bidle '38
W. S. Bidle Co.
Cleveland

Walter Mathesius '36
Carnegie-Illinois Steel Corp.
Chicago

Paul D. Merica '36
International Nickel Co.
New York

METALS HANDBOOK COMMITTEE

C. H. HERTY, JR., Chairman '36
Bethlehem Steel Co.
Bethlehem

G. C. Riegel '37
Caterpillar Tractor Co.
Peoria

S. L. Hoyt '38
A. O. Smith Corp.
Milwaukee

W. D. Halsey—A.W.S. Rept.
Jerome Strauss, A.I.M.E. Rept.
J. E. DONNELLAN, Secretary

R. L. Dowdell '38
University of Minnesota
Minneapolis

W. C. Chancellor '37
National Tube Co.
Lorain, Ohio

J. P. Gill '36
Vanadium-Alloys Steel Co.
Latrobe, Pa.

Adam Steever '37
Lindberg Steel Treating Co.
Chicago

PUBLICATION COMMITTEE

W. P. SYKES, Chairman '36
General Electric Co.
Cleveland

H. E. Ardahl '37
Deere & Co.
Moline

C. L. Clark '36
University of Michigan
Ann Arbor

C. N. Dawe '38
Vanadium Corp. of America
Detroit

W. E. Harvey '37
J. A. Roebling & Sons
Trenton

G. V. Luerssen '36
Carpenter Steel Co.
Reading

O. W. McMullan '38
International Nickel Co.
Bayonne

N. I. Stotz '38
Cyclops Steel Co.
Titusville

RAY T. BAYLESS, Secretary

A. A. Bates '38
Case School of Applied Science
Cleveland

E. S. Davenport '37
U. S. Steel Corp.
Kearny, N. J.

M. A. Grossmann '37
Carnegie-Illinois Steel Corp.
Chicago

Louis Jordan '36
Bureau of Standards
Washington

D. F. McFarland '37
Pennsylvania State College
State College, Pa.

R. F. Mehl '36
Carnegie Institute of Technology
Cambridge, Mass.

Joseph Winlock '37
E. G. Budd Mfg. Co.
Philadelphia

Table of Contents

The Importance of Aluminum Additions in Modern Commercial Steels—
By Harry W. McQuaid 797

Hardening Characteristics of One Per Cent Carbon Tool Steels—
By T. G. Digges and Louis Jordan 839

Discussion 856

Interpretation of Torsion Impact Properties of Carbon Tool Steel—
By G. V. Luerssen and O. V. Greene 861

Discussion 878

Contributory Effects of Furnace Atmospheres on the Grain-Size of Molybdenum High Speed Steel—By Arthur Phillips and M. J. Weldon 886

Discussion 905

Correlation of Failures from Embrittlement of 4 to 6 Per Cent Chromium Steel with the Notched Bar Impact Test—By H. M. Wilten 915

Discussion 939

Chromium Steels of High Nitrogen Content—By Russell Franks 968

Discussion 987

Influence of Carbon Content on High Temperature Properties of Steels—
By A. E. White, C. L. Clark and R. L. Wilson 995

Discussion 1015

A New Heat Resistant Alloy—By S. L. Hoyt and M. A. Scheil 1022

Discussion 1039

The Aging of Steel—By E. S. Davenport and E. C. Bain 1047

Discussion 1096

The Orientation of Crystals in Silicon Iron—By Richard M. Bozorth 1107

Technical Program and Reports of Officers—Seventeenth Annual Convention of the Society 1112

Statement of the ownership, management, circulation, etc., required by the act of congress of August 24, 1912, of TRANSACTIONS of the American Society for Metals, published quarterly at Cleveland, Ohio, for October 1, 1935, State of Ohio, county of Cuyahoga, ss. Before me, a notary public, in and for the state and county aforesaid, personally appeared Ray T. Bayless, who, having been duly sworn according to law, deposes and says that he is the editor of the TRANSACTIONS of the American Society for Metals, and that the following is, to the best of his knowledge and belief, a true statement of the ownership, management, etc., of the aforesaid publication for the date shown in the above caption, required by the Act of August 24, 1912, embodied in section 411, Postal Laws and Regulations to wit:

1.—That the names and addresses of the publisher, editor, managing editor, and the business managers are: Publisher, American Society for Metals, 7016 Euclid Avenue, Cleveland, Ohio; Editor and Managing Editor, Ray T. Bayless, 7016 Euclid Avenue, Cleveland, Ohio; Business Manager, W. H. Eisenman, 7016 Euclid Avenue, Cleveland, Ohio.

2.—That the owner is: The American Society for Metals, 7016 Euclid Avenue, Cleveland, Ohio, which is an educational institution, the officers being: President, B. F. Shepherd; Vice-president, R. S. Archer; Secretary, W. H. Eisenman; Treasurer, Emil Gathmann; Directors, W. H. Phillips, E. C. Bain, W. P. Woodside, Walter Mathesius, George B. Waterhouse. All above officers of the American Society for Metals, address at 7016 Euclid Avenue, Cleveland, Ohio.

3.—That known bondholders, mortgagees and other security holders are: none.

4.—That the two paragraphs next above, giving the names of the owners, stockholders and security holders, if any, contain not only the list of stockholders and security holders as they appear upon the books of the company but also, in cases where the stockholder or security holder appears upon the books of the company as trustee or in any other fiduciary relation, the name of the person or corporation for whom such trustee is acting, is given; also that the said two paragraphs contain statements embracing affiant's full knowledge and belief as to the circumstances and conditions under which stockholders and security holders who do not appear upon the books of the company as trustees, hold stock and securities in a capacity other than that of a bona fide owner; and this affiant has no reason to believe that any other person, association, or corporation has any interest direct or indirect in the said stock, bonds, or other securities than as so stated by him. Ray T. Bayless, managing editor, sworn to and subscribed before me this 11th day of October, 1935.

(Seal) Arthur T. Wehrle, notary public.

(My commission expires January, 1938.)

"TOOL STEELS"

A Series of Five Educational Lectures on the Selection, Properties and Uses of Commercial Tool Steels

by JAMES P. GILL

Chief Metallurgist

VANADIUM-ALLOYS STEEL CO., LATROBE, PENNA.

This five-lecture series constituting a most outstanding piece of work by an expert in the tool steel industry, will make a valuable addition to your library. These lectures were presented at the Sixteenth Annual Meeting of the Society in New York City, October 1 to 5, 1934, and are now made available to the entire membership. This is a book containing 136 pages and is neatly bound in cloth. It is available in paper cover also.

Price: Cloth bound, $2.50—Paper bound, $2.00

CONTENTS:

Lecture I. Manufacture, Classification and Selection of Tool Steels

a. History
b. Manufacture
Melting, forging, annealing and inspection
c. Classification
d. Selection
Correlation of physical properties and requirements of applications

Lecture II. Evaluation and Testing: Effect of Alloying Elements

a. Evaluation
Shop test, quality and physical properties
b. Testing
Tensile properties, hardenability, fracture, macro and microscopic tests
c. General effect of Alloying Elements
C, S, P, Mn, Si, Ni, Cr, V, Cr-V, W, Mo
d. Specific Effect of Alloying Elements on Hardenability

Lecture III. Carbon and Low Alloy Tool Steels

a. Straight Carbon Tool Steels
b. Carbon Vanadium Tool Steels
c. Carbon Tool Steels with Less than 1.00% of Alloying Element
d. High Carbon, Low Tungsten Tool Steels
e. Manganese Oil Hardening Tool Steels

Lecture IV. Tool Steels of Intermediate Alloy Content

a. Low Carbon, Low Tungsten Types
b. Finishing Steels
c. Silicon-Manganese Steels
d. Die Steels for Hot Work
Chrome die steels, tungsten steels and chrome-tungsten steels for hot work, miscellaneous types

Lecture V. High Carbon, High Chromium Steels and High Speed Steels

a. High Carbon, High Chromium Steels
Air hardening types, oil hardening types
b. High Speed Steels
18-4-1 types, 18-4-2 types, 14-4-2 types, cobalt types, miscellaneous types

Send your check or money order to the

American Society for Metals

7016 Euclid Avenue — Cleveland, Ohio